THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS
AND OTHER ANALYTICAL CHEMISTS

A JOINT Meeting of the Society and the Food Group of the Society of Chemical Industry was held at 7 p.m. on Wednesday, December 5th, 1951, in the Meeting Room of the Chemical Society, Burlington House, London, W.1. The Chairman of the Food Group, Professor H. D. Kay, C.B.E., D.Sc., F.R.S., having opened the proceedings invited the President, Dr. J. R. Nicholls, C.B.E., F.R.I.C., to occupy the Chair for the remainder of the meeting.

The meeting took the form of a Discussion under the general title "The Food Standards Issue—What Does the Future Hold?" with the following special contributions: "Compositional Standards," by T. McLachlan, D.C.M., A.C.G.F.C., F.R.I.C.; "Microbiological Standards," by C. L. Heller, Ph.C., M.I.Biol.

NEW MEMBERS

Charles Fulton Allister, B.Sc. (Lond.), F.R.I.C., A.H.-W.C.; William George Batt, D.Sc. (Philadelphia); Derrik Bolton, B.Sc. (Lond.); Sigmund Folkvord, D.Tech. (Trondheim); Frederick Holmes, B.Sc. (Lond.), A.R.I.C.; Derek Bernard Schaverien, B.Sc. (Lond.); Adolph William Henry Upton, A.C.G.F.C., F.R.I.C.

DEATH

WE regret to record the death of

Ernest Walter Wright

Some Observations on the Determination of the Activity of Rennet

BY N. J. BERRIDGE

(Presented at the meeting of the Society on Wednesday, November 7th, 1951)

Experiments on the measurement of the clotting time of rennet in a substrate made by reconstituting skimmed milk powder in 0·01 M calcium chloride are described in detail, as is the method of observing the clotting-point in a thermostatically controlled enclosure.

The reproducibilities of activities of rennet so determined are tabulated and it is shown that differences of 2 per cent. between samples should be recognisable. Comparisons have been made between the clotting times in calcified milk and in bulk milk to show the suitability of the artificial substrate for the assay of rennet for cheesemaking.

It is suggested that either dry powdered rennet or a special batch of milk powder could be used as a standard.

LARGE quantities of rennet are used in the manufacture of cheese and it is the only enzyme to be sold widely by retail. The determination of rennet strength and the standardisation of rennet are, therefore, important. The technique of measurement described below was used in work that culminated in the crystallisation of rennin[1] and it is hoped that the method will assist in the solution of the problems of standardisation. The enzymic activity of a rennet

solution may be determined by measuring the time taken by a given volume to clot a given volume of milk; but in order to obtain reproducible values each of the many variables in the process of clotting must be adequately controlled and certain precautions are necessary on account of the nature of both enzyme and substrate.

The precautions to be observed with rennet differ but little from those required by enzymes in general. For example, its destruction must be avoided during dilution and assay and the activation of any pro-rennin that may be present must be prevented. This activation may be rapid in dilute, slightly acid, solution and if a rising activity is observed in a series of replicates it is necessary to make fresh dilutions at a controlled pH value of, say, 6 to 7.

Although the rennet itself introduces no unusual difficulties, the substrate requires particular care and attention because of the complex and variable nature of milk, the clotting of which is not a direct result of the action of the enzyme but of a secondary reaction that appears to follow the enzymic reaction after a time lag. The variations in the reactivity of milk may be partly obviated by making special casein preparations, but this introduces further difficulties and it is better, in general, to use a good quality milk powder, prepared from skim milk with the minimum of heating, from which a more reproducible substrate for rennet testing can be prepared; although the readiness with which the reconstituted milk clots is liable to vary with the age of the powder and with the conditions of storage. This variation is largely due to changes of state in the calcium phosphate between the ionised and the colloidal condition.[2] These changes can to some extent be prevented by adding an excess of calcium ions, and milk prepared by reconstituting a powder in 0·01 M calcium chloride was stable enough for use as a substrate.

The time lag between the enzymic change and the clotting can be a serious source of error because it may be unnoticed and can vary with the history of the milk and with the conditions of the test. The existence of the time-lag is made evident by lack of linearity between the clotting time and the concentration of rennet, and also by a point being reached beyond which further increases in the concentration of rennet fail to reduce the clotting time.

The time-lag, or period of time between the action of the rennet and the non-enzymic change that causes clotting, is influenced by temperature and the concentration of electrolytes in the milk; it can be considerably shortened by reconstituting the skimmed-milk powder with 0·01 M calcium chloride solution instead of distilled water.

The non-linearity mentioned above is diminished, but not entirely removed, by reconstituting in calcium chloride; and, as other factors in the milk probably have some effect, it is necessary with a new substrate to plot a graph of enzyme concentrations against reciprocal clotting times in order to determine the range of clotting times over which linearity may be assumed to hold good without significant error.

OBSERVATION OF THE CLOTTING-POINT

The precise observation of the moment of clotting is a little difficult. Various kinds of apparatus have been devised to facilitate it.[3,4,5] The visual method described here has the advantage of needing only simple apparatus that is readily available and easily cleaned. It gives, moreover, a particularly sharp end-point; the little skill required is readily acquired with practice.

METHOD

APPARATUS—

　　A stop-watch.
　　Volumetric apparatus for diluting the rennet.
　　Test tubes—These should hold approximately 20 ml to the brim.
　　Glass rods—These should be 3 to 4 inches longer than the test tubes.
　　A "barrel-and-plunger" whisk for reconstituting the milk.
　　A rapid measuring device—This is required for dispensing 10-ml quantities of milk, and may be, *e.g.*, an ordinary 10-ml pipette with a wide tip. The pipette used in this work had a delivery time of about 4 seconds and an accuracy of ±0·1 per cent. with water and of ±0·2 per cent. with milk.
　　A water-bath controlled at 30° ± 0·2° C—This should be made of glass, or fitted with a transparent front, and provided with a rack suitable for holding at least 9 test tubes in batches of 3 and a convenient clamp for holding one tube at a time near the glass front for observation of the clotting-point.

The tube should be illuminated by a 100-watt electric lamp placed in front of the water-bath, just above and slightly to the left of the operator. The lamp should be shielded so that the test tube is brilliantly lit, but neither direct light nor reflection from the glass should dazzle the operator. The background behind the tube should be as dark as possible. These conditions are necessary for accurate observation and to prevent fatigue, which leads to inaccuracies.

Like many other proteins, rennin tends to be adsorbed on glass surfaces. Cleanliness of all glassware is therefore particularly important and soaking in strong sulphuric acid - bichromate mixture followed by thorough rinsing, first with tap water and then with distilled water, is essential.

REAGENTS—

Calcium chloride solution—This should be accurately adjusted to 0·01 M.

Spray-dried skim milk powder—This should be prepared without pre-heating. (The powder used in this work was supplied by Messrs. Aplin and Barrett Ltd., Yeovil, Somerset.)

PROCEDURE—

All weighings and volume measurements should be made with errors not greater than $\pm0·3$ per cent. This wide latitude is permissible because of the, so far, unavoidable variations in the clotting times.

Weigh 12·0 g of the milk powder and reconstitute with 100 ml of the 0·01 M calcium chloride solution. Pipette 10·0 ml of the "milk" into a number of test tubes and place them, in batches of three, in a suitable rack in the water-bath at intervals of 15 minutes between each batch. Since the clotting time with a constant rennet concentration changes slightly with the time during which the milk is warmed, this time is kept approximately constant at 30 to 35 minutes. Thus, after the first half-hour there will be a batch of tubes ready for use every 15 minutes as long as the supply is maintained. If the approximate activity of the rennet is not known, make a preliminary dilution to give, on the basis of an assumed activity, a clotting time of 1 to 2 minutes and use the first batch of tubes to obtain an approximate figure for the clotting time. From this figure, calculate by simple proportion the dilution necessary to give a clotting time of about 5 minutes. (The actual range of clotting time permissible will depend on the length of the linear portion of the graph, as mentioned in the introduction.) Make this new dilution with distilled water not more than 5 minutes before the milk is ready for use. Now clean the thumb of the right hand thoroughly, dry it on a clean cloth and take care not to contaminate it with rennet during the test. When the milk is ready, add to one of the tubes 1·00 ml of the rennet dilution in such a way that it runs down the side of the tube to form a layer on the surface of the milk, close the tube with the cleaned thumb, and mix by inversion, starting the stop-watch simultaneously. Repeat the inversion and reversion twice more to wash all the rennet from the side of the test tube. Repeat the whole procedure with the second tube of the set, timing the first inversion to coincide with a reading of 60 seconds on the stop-watch, and do so similarly with the third, mixing it at 120 seconds. About 1 minute before the expected end-point in the first tube, insert a clean stirring rod and clamp the tube firmly so that the level of the milk is well below that of the water in the bath and the tube wall above the milk is clearly visible. After stirring thoroughly for a few seconds, raise the rod until its lower end touches the side of the test tube 1 or 2 cm above the surface of the milk and hold it in that position to allow a thin film of milk to run from it over the inner surface of the tube. Give the rod a vertical jerk at intervals of 1 or 2 seconds to assist the flow of the milk film from the reserve held by surface tension between the end of the rod and the wall of the test tube. Just before this supply of milk is exhausted, spread the remaining milk towards the side of the tube and repeat the operation on a fresh but easily visible section of the test tube. Watch the old film until the new one is properly established. Keep the film flowing continuously but as thinly as possible so as to be only just visible; clotting is then easily observed as the sudden appearance of heterogeneity, the faint grey film breaking up into white particles on a black background. During this observation place or hold the stop-watch only just out of sight so that the instant clotting takes place a slight movement of the eyes enables the time to be observed within a second. Immediately transfer the rod to the second tube and repeat the above procedure. Similarly determine the third clotting time and stop the watch. In this way clotting times are obtained in triplicate.

With routine samples it is convenient for one worker to assay 4 samples per hour.   Larger quantities of "milk" may then be made at one time, providing its properties do not change before use.   The "milk" used in this work was stable for several hours at room temperature.

The strength of the rennet may be expressed in arbitrary units per given volume by dividing the dilution used by the mean clotting time in seconds, and when a sufficient number of samples have been measured the replicate clotting times can be used to estimate the standard error by the analysis of variance in the usual way.

RESULTS

The reproducibility of activities determined by the method described is shown in Table I. Twenty-three rennet samples were diluted equally and assayed in triplicate.   The mean clotting time for the least active was 419 seconds, that for the most active, 311 seconds. The average value of all the means was 358 seconds and the standard error of each mean was 3·8 seconds.   Similar sets were assayed 7 and 9 months later.   The three sets of results are

TABLE I

STANDARD ERRORS OF RENNET ASSAYS

				Average of the mean clotting times (average of 23 means)	Range of the mean clotting times (means of 3 observations)	Standard errors of the mean clotting times
				(seconds)	(seconds)	(seconds)
Set 1	..	..	..	358	311–419	3·80
Set 2	..	..	..	147	131–167	1·35
Set 3	..	..	..	191	161–242	1·29

collected in Table I, in which the first two columns indicate the spread of values due to the differences between the rennet samples, but the standard error in the last column reflects only the unavoidable variations in the clotting times when the rennet is kept constant.   The diminution in the standard errors compared with the actual values of the means reflects the increasing skill of an assistant who was new to the test when the first batch of assays was done.   Taking the last value of 1·29 for the standard error and a probability limit of 0·05 as an example, the minimum significant difference between 2 means, each of 3 clotting times, becomes 3·7 seconds.   Comparing this with clotting times of the order of 200 seconds, it is clear that differences of 2 per cent. between samples will usually be recognisable.

In order to get some idea of the suitability of this substrate for the assay of rennet for cheesemaking, the activities of a number of enzyme preparations in bulk milks before and after pasteurising and after ripening in the cheese vat were compared with their activities in the calcified milk.   The results are shown in Table II, in which the figures in the main section are ratios.   Each figure was obtained by dividing the calculated clotting time of the particular enzyme in calcified milk by the calculated clotting time of the same enzyme at the same concentration in the bulk milk indicated.   All the rennets were diluted to give clotting times of 5 to 8 minutes whatever the milk in use; corresponding times at a rennet concentration of 0·1 per cent. were then obtained by simple proportion to facilitate the calculation of the ratios.   The four rennet preparations differed in the method of manufacture.   It is rather remarkable that the calcified milk also behaved so much like bulk milk towards pepsin and papain.

An alternative substrate consisting of milk powder reconstituted with phosphate buffer was tried at the same time.   This clotted with rennin more slowly than bulk milk, so that most of the ratios were between 5 and 10, and even slower with pepsin, for which the ratios rose to 11·6, but it clotted more quickly with papain, giving ratios from 0·5 to 0·8.

It can be seen from the table that there were some samples that responded differently to the different rennets; for example, milks Nos. 1 and 2 behaved similarly to all four rennets, but for milk No. 3 the ratio for the first rennet does not agree with those for the other three rennets.   For other samples, smaller differences will be noticed and it is clear that these discrepancies are not of practical importance.

DISCUSSION OF RESULTS

Although the rate of clotting of milk is sensitive to the pH value there is no point in buffering the milk, for its buffering power is already very high compared with the minute

quantities of acid that may be added with normal rennet.   Cheesemaking rennet, for example, needs diluting several hundred times before testing.   However, if very dilute rennet preparations are to be assayed, the role of acidity must be remembered.   The variations between different milk powders are also partly due to differences in acidity, but it is a simple

TABLE II

THE RATIOS $\dfrac{\text{CLOTTING TIME IN CALCIFIED MILK}}{\text{CLOTTING TIME IN BULK MILK}}$

RAW MILK

Rennet No.	Milk No.	1	2	3	4	5	6	7
	Acidity*	0·23	0·21	0·21	0·20	0·20	0·20	0·20
1		1·43	1·17	1·40	1·13	0·93	1·09	1·21
2		1·46	1·21	1·08	1·12	0·97	1·02	1·23
3		1·46	1·23	1·08	1·08	0·93	1·14	1·35
4		1·46	1·22	1·07	1·10	0·90	0·99	1·18
Pepsin		1·29	0·98	—	—	—	—	—

PASTEURISED BULK MILK, H.T.S.T.

	Milk No.	8	9	10	11	12	13
	Acidity*	0·21	0·19	0·22	0·20	0·22	0·21
1		1·22	1·07	1·42	1·13	1·67	1·20
2		1·21	1·08	1·40	1·09	1·57	—
3		1·21	1·08	1·35	1·10	1·63	1·20
4		1·26	1·12	1·46	1·07	1·64	1·17
Papain		—	—	—	1·15	1·09	0·70
Pepsin		1·07	—	1·32	—	—	—

DIRECT FROM CHEESE VAT JUST BEFORE RENNETING

	Milk No.	14	15	16	17	18	19
	Acidity*	0·19	0·18	0·19	0·19	0·19	—
1		1·05	0·73	0·84	0·86	0·83	0·75
2		0·95	0·72	0·83	0·85	0·82	0·74
3		0·98	0·73	0·82	0·84	0·82	0·73
4		0·97	0·73	0·85	0·86	0·85	0·74

CLOTTING TIMES FOR CALCIFIED MILK
Calculated to 0·1 per cent. concentration of the enzyme preparation

Rennet No.	1	2	3	4	Papain	Pepsin
Time, seconds	220	168	81	78	7500	88

* Titratable acidity as percentage of lactic acid determined by the creamery.

matter to compare a fresh batch of standard milk powder with the old and calculate a correction factor.   Frost[6] has succeeded in diminishing this change in sensitivity of the substrate with a new batch of milk powder by including acetate buffer in the liquid for reconstitution.   This suggests that a further improvement might be effected by buffering the calcium ion activity with a partly ionised calcium salt.   The work of Pyne[7] shows that calcium citrate would probably be suitable.   The other ionic constituents also play their part.   For example, when 1 per cent. of sodium chloride was added to a diluted rennet and 1 ml was added to 10 ml of milk, the clotting time was increased by 8 per cent.   These errors will arise when rennet solutions of low activity are being tested.

A further step towards standardisation can be made by using dry powdered rennet as a standard.   In fact, two master standards could be maintained, a special batch of milk powder and a special batch of rennet powder.   Over a limited period a rennet powder has been used as a standard.   No variation in the sensitivity of the substrate during this time was noticed. It appears to be the general opinion that dried rennet is particularly stable.   See, for example, Havenhill.[8]

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DISCUSSION

THE PRESIDENT congratulated the author on the skill with which he had tackled the essentially biological problem of the activity of rennet.

DR. J. G. DAVIS said that he was particularly interested in the apparent lack of systematic behaviour of the four samples of rennet with ordinary raw and pasteurised milks, in contrast to which the relative behaviour of all four rennets with cheese-making milk seemed remarkably consistent. He asked whether the bulking of the ordinary raw and pasteurised milks was as great as that of the cheese-making milk; presumably the bulks of the latter would have been at least 750 or 1000 gallons. Otherwise the only difference appeared to be that, if the cheese-making milks were tested at rennetting time, the pH would be slightly lower at about 6·4.

DR. BERRIDGE said that the raw milk consisted of drip samples taken from a junction in the pipeline supplying the pasteuriser. Pasteurised samples were taken in a similar way out of milk flowing away from the pasteuriser. This seemed the nearest possible approach to truly representative bulk samples, and it seemed likely that the lower pH value of the ripened milks made them behave more uniformly towards rennet.

MR. P. J. GOODE asked whether the author could advise on the storage of dried milk powder. His experience had been that, after a few weeks, dried milk kept in large tins would not set when reconstituted and treated with rennet. Keeping the milk in small, brim-full, airtight cans had no apparent effect on the storage life. He also asked if the author could give him some information about variations in clotting time with different types of milk, *e.g.*, pasteurised, unpasteurised and homogenised, and with large variations of fat content up to about 20 per cent., such as a housewife might use when taking the "top off the milk" for her junket.

DR. BERRIDGE replied that no trouble had been experienced with the storage of milk powder. Indeed, it was partly because its stability seemed too good to be true that dried rennet was used as a confirmatory standard. The quality of the dried milk appeared to be the controlling factor; if a batch seemed to be unstable, it should be discarded. It was well known that pasteurising increased the clotting time of milk, but homogenising had no effect, and variations in fat content had only the small effect that results from the corresponding change in the proportion of aqueous phase present.

MR. A. L. BACHARACH suggested that the use of a freeze-dried "standard preparation" of rennet, which could probably be prepared in sufficient quantities to last a large number of people for a long time, might compensate for variations in behaviour of different samples of milk powder, especially under the standardised conditions Dr. Berridge had laid down. It would not then be necessary, and would indeed probably involve practical difficulties because of the amounts of substrate required, to prepare large quantities of "standard" milk powder, for each fresh batch of this could be checked against the standard rennet, which could also be used for comparison with the "test samples" of rennet coming up for assay. The procedure would be strictly analogous to that of using a standard vitamin preparation and a variable rat colony.

DR. BERRIDGE thanked Mr. Bacharach for his valuable suggestion.

DR. J. H. HAMENCE congratulated the author on the method, and said that he himself had used calcium ions in the form of calcium chloride to assist in clotting reconstituted dried milk and had found the technique to work very well. In view of the difficulty of obtaining sufficient quantities of dried milk powder he asked the author if he could give him any idea of the maximum range of variation that was likely to occur between different batches of dried milk.

DR. BERRIDGE replied that the milk powders used for some of the illustrative data showed that variations could be very great. On the one hand there was milk, dried without pre-heating, that clotted readily without additional calcium ions, and with calcium gave a straight-line response over a wide range of rennet concentrations; on the other hand there was milk that hardly clotted at all unless calcium ions were added, and even then the straight-line response was limited to a narrow range of rennet concentrations. These variations could doubtless be reduced by selecting the milks.

The Determination of 2:4-Dichlorophenoxyacetic Acid

By S. W. STROUD

A rapid and accurate method is described for the separation and determination of 2:4-dichlorophenoxyacetic acid in a mixture of chlorinated phenoxyacetic acids. It is based on the separation of the acids by partition chromatography between ether and strong phosphate buffers on a kieselguhr column and their determination by titration of the carboxylic acid groups. In this way an accurate determination of the individual acids in a mixture of chlorinated phenoxyacetic acids can be made on 10 to 20 mg of a sample.

THE use of chlorinated phenoxyacetic acids as plant-growth regulating substances and as selective herbicides has become well established, the most widely used of the group being 2:4-dichlorophenoxyacetic acid (2:4-D). Several reviews on the relative activities of this group of compounds have been published and it has been shown that, although the 2-chloro- and 4-chlorophenoxyacetic acids are active, they are less so than 2:4-D and 2:4:5-trichlorophenoxyacetic acid (2:4:5-T); 2:4:6-trichlorophenoxyacetic acid (2:4:6-T) is inactive.

Despite the extensive use of 2:4-D, no satisfactory simple chemical method has been described for its determination in a complex mixture. Bandurski[1] described a method based on the spectrophotometric determination of 2:4-D in soil extracts, but the method was not specific for 2:4-D. Freed[2] used a sensitive colorimetric method, chromotropic acid being used for the detection of 2:4-D, but again the method was not specific and proved unsuitable for the determination of 2:4-D. Other methods used for the determination of 2:4-D involve the estimation of the total chlorine content followed by titration of the carboxylic acid group. Details of such methods have been given by Rooney[3] and Heagy.[4] These authors point out, however, that the methods described are not entirely satisfactory, as estimations involving total chlorine content will give erroneous results if other chlorine compounds are present; likewise the estimation by titration of the acid group by the methods stated will also include other organic acids that may be present. It can be seen that the presence of other chlorine-substituted phenoxyacetic acids would falsify the results; for example, an equimolecular mixture of 4-chlorophenoxyacetic acid and 2:4:6-trichlorophenoxyacetic acid would analyse by these methods as 2:4-D.

For the accurate estimation of 2:4-D it is necessary, therefore, to ensure a complete separation of the 2:4-D from the related compounds that may be present, by virtue of the method of preparation, in the product used for horticultural purposes. A method of separation and estimation of 2:4-D has been described by Warshowsky and Schantz,[5] but the method involves the use of the Craig counter-current extraction machine followed by the spectrophotometric determination of the 2:4-D in the selected tubes.

It has been found that the separation of 2:4-D from the other chlorinated phenoxyacetic acids can be rapidly and effectively accomplished by means of partition chromatography between ethyl ether and strong phosphate buffer, advantage being taken of the differences in the pK values and partition coefficients of the various acids. By this means it has proved possible to separate 2-chloro-, 4-chloro-, 2:4-dichloro- and 2:4:6-trichlorophenoxyacetic acids from a mixture of them all and to estimate them separately by titration. Whilst 2:4:6-trichlorophenoxyacetic acid and 2:4-D can be individually separated and estimated in one procedure with a buffer at pH 6·35, under these conditions 4-chloro- and 2-chlorophenoxyacetic acids remain on the column and are not eluted. For a complete analysis, therefore, a further separation is required, at pH 5·80, to separate 2-chlorophenoxyacetic acid and 4-chlorophenoxyacetic acid and to allow them to be determined separately.

The method given below can be used for the determination of the salts, amides, esters, and so on, of 2:4-D and for their determination in horticultural preparations after the liberation of the free acid by the usual methods.

METHOD

APPARATUS—

A chromatographic tube, which is a glass tube of length 40 cm and diameter 1·2 cm, closed at one end by a perforated silver disc covered with a filter-paper disc.

A separating funnel, fitted with a cork to fit the open end of the column, to act as a reservoir for the eluting solvent.

MATERIALS AND SOLUTIONS—

Kieselguhr, "Hyflo-Supercel"—This material* is suitable for use without pre-treatment.

Sodium phosphate buffer A—A 25 per cent. v/v solution of sodium phosphate buffer adjusted to pH 6·35 and prepared as follows. Add sufficient of a 30 per cent. w/v aqueous
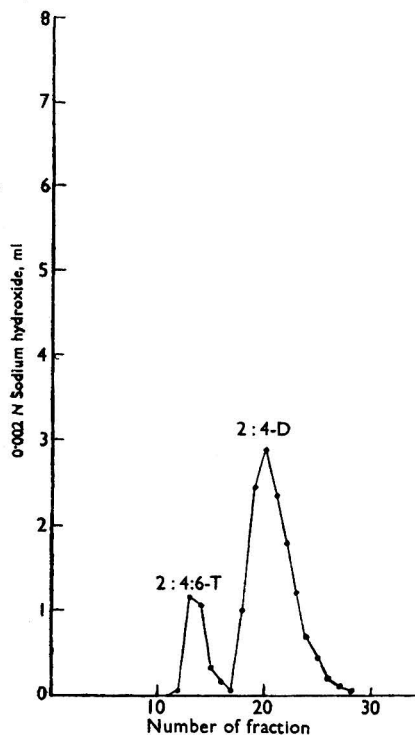
Fig. 1. The separation of 2 : 4 : 6-trichlorophenoxyacetic acid and 2 : 4-dichlorophenoxyacetic acid by means of phosphate buffer, pH 6·35
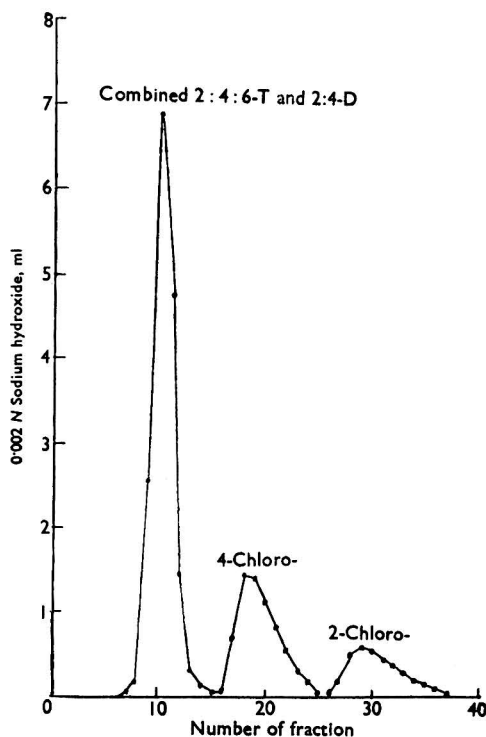
Fig. 2. The separation of 4-chloro- and 2-chlorophenoxyacetic acids from the combined 2 : 4 : 6-trichloro- and 2 : 4-dichlorophenoxyacetic acids by means of phosphate buffer, pH 5·80

solution of sodium hydroxide to a saturated aqueous solution of sodium dihydrogen phosphate to bring the solution to approximately pH 6·35. Cool and allow the solution to stand overnight to avoid supersaturation. Then add just sufficient water to redissolve any precipitate and dilute the resulting solution with three times its volume of distilled water. Adjust this solution accurately to pH 6·35 by adding either 10 per cent. w/v aqueous phosphoric acid solution or 10 per cent. w/v aqueous· sodium hydroxide solution.

Sodium phosphate buffer B—A 25 per cent. v/v solution of sodium phosphate buffer prepared as for buffer A, but adjusted at all stages to pH 5·80.

Ether—Sp.gr. 0·720, equilibrated with the appropriate buffer solution.

Sodium hydroxide solution—0·002 N.

Bromothymol blue solution—0·01 per cent. w/v.

* Supplied by Messrs. Johns-Manville Co., Ltd., Artillery House, Artillery Road, London, S.W.1.

PROCEDURE FOR THE SEPARATION AND DETERMIMATION OF 2:4:6-T AND 2:4-D—

Mix intimately 15 g of kieselguhr and 7·5 ml of sodium phosphate buffer A, pH 6·35, and pack the mixture dry into the chromatographic tube. Displace the air in the column by running through a quantity of ether, previously equilibrated with the buffer solution.

TABLE I

ANALYSIS OF MIXTURES OF CHLORINATED PHENOXYACETIC ACIDS

Mixture	Compounds present	Weights taken, mg	Titration sum, ml	Weights found, mg	Recovery, %
A	2:4:6-T	2·00	3·85	1·967	98·4
	2:4-D	5·00	11·30	4·995	99·9
B	2:4:6-T	1·00	1·95	0·996	99·6
	2:4-D	7·50	16·85	7·448	99·3
C	2:4:6-T	2·00	3·90	1·992	99·6
	2:4-D	5·00	11·20	4·950	99·0
	4-chloro-	2·00	5·30	1·977	98·9
D	2:4-D	5·00	11·20	4·950	99·0
	4-chloro-	5·00	13·35	4·980	99·6
	2-chloro-	5·00	13·90	5·185	103·7
E	2:4-D	5·00	11·25	4·972	99·4
	4-chloro-	2·00	5·30	1·977	98·9
	2-chloro-	3·00	8·10	3·021	100·7
F	2:4:6-T	2·16	4·15	2·121	98·2
	2:4-D	6·95	15·65	6·917	99·5
	4-chloro-	2·13	5·75	2·145	100·7
	2-chloro-	3·34	8·90	3·320	99·4
G	2:4:6-T	1·40	2·75	1·405	100·4
	2:4-D	5·85	13·20	5·834	99·7
	4-chloro-	2·40	6·50	2·425	101·0
	2-chloro-	1·30	3·40	1·268	97·6

Place on the column 2 ml of an ether solution of the material under test, which should contain approximately 10 mg of 2:4-D, and apply gentle air pressure to the top of the column to force the solution into the kieselguhr mixture. Apply two further 1-ml portions of ether to the column in a similar manner to ensure that all of the material is on the column before the elution is begun. Then fix the separating funnel, filled with the ether, to the open end of the tube and perform the elution, using gentle air pressure to speed the flow through the column.

Take successive 2·5-ml fractions of the eluate, add 2 ml of distilled water and 2 drops of bromothymol blue indicator solution to each fraction and titrate with 0·002 N sodium hydroxide solution to the blue-green shade of the indicator. Deduct the blank value, which is obtained by titrating 2·5 ml of the ether solution used for the elution under the same conditions as above, and plot the corrected titration figures against the number of the fraction and draw the graph.

To ensure the complete elution of the 2:4-D from the column, a total of thirty fractions is required. A typical graph obtained is shown in Fig. 1, two peaks corresponding to the 2:4:6-T and 2:4-D contents being obtained. Under the above conditions the 4-chloro- and 2-chlorophenoxyacetic acids remain on the column.

To determine the weight of the acid represented by an individual peak, the corrected titration figures corresponding to all the points determined on that peak are summed and the sum is multiplied by the appropriate factor to give the weight of the acid in mg; e.g., if V_1 and V_2 are the respective sums of the titration figures corresponding to the points on the 2:4:6-T and 2:4-D peaks in ml of 0·002 N sodium hydroxide, then—

the weight of 2:4:6-T $= V_1 \times 0·511$ mg,
and the weight of 2:4-D $= V_2 \times 0·442$ mg.

This separation is sufficient for the determination of 2:4-D in a mixture.

PROCEDURE FOR THE SEPARATION AND DETERMINATION OF 4-CHLORO- AND 2-CHLOROPHENOXY-
ACETIC ACIDS—

Pack the column dry as before with a mixture of 15 g of kieselguhr and 7·5 ml of sodium
phosphate buffer B, pH 5·80.   Apply the same load to the column as for the separation of
2:4:6-T and 2:4-D and take forty fractions; titrate as before and draw the graph (see Fig.2).
Under these conditions the 2:4:6-T and 2:4-D are eluted together as one peak, followed by
the peaks corresponding to the 4-chloro- and 2-chloro- compounds.

If V_3 and V_4 are the respective sums of the titration figures corresponding to the points
on the latter peaks in ml of 0·002 N sodium hydroxide, then—

the weight of 4-chlorophenoxyacetic acid   = $V_3 \times 0·373$ mg,
and the weight of 2-chlorophenoxyacetic acid = $V_4 \times 0·373$ mg.

RESULTS

The results shown in the table below have been obtained from the analysis of a series of
mixtures of the various chlorinated phenoxyacetic acids.   Figs. 1 and 2 show the graphs
obtained from mixture G.

From the results obtained it can be seen that the method is capable of the separation
and determination of 2:4-D and the other constituents with a high degree of accuracy.

By decreasing the cross-section of the tube, maintaining the same length, and by using
a more dilute solution of sodium hydroxide and micro-burettes, it is possible to carry out
the analysis on smaller quantities of materials, which should render the method suitable for
estimations on soil extracts.

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DISCUSSION

THE PRESIDENT remarked on the neatness of this technique, which doubtless would find many other
applications.

MR. N. HERON suggested that an indicator could be adsorbed on the column, and so allow the flow
of the acids to be followed readily.

MR. STROUD said that it was doubtful whether there was any practical advantage in using an indicator
adsorbed on the column to make the various bands visible.   His colleague, Mr. P. B. Baker, had established
a rapid paper-chromatographic method for the qualitative analysis of chlorinated phenoxyacetic acid
mixtures with the same buffer - ethyl ether systems, and he used a methyl red spray for the detection of
the bands.

MR. A. L. BACHARACH asked whether any advantage had been found in using a system of automatic
or semi-automatic "cut-takers."

MR. STROUD replied that the use of an automatic or semi-automatic fraction cutter, where available,
was an advantage provided that sufficient care was taken in the design of the syphon system in the apparatus
to ensure satisfactory working when ethyl ether was the eluting solvent.   As the total number of cuts and
the time taken for the estimation were both small, manual manipulation was easy.

MR. K. GARDNER asked whether phenol and its chlorinated derivatives preceded the phenoxyacetic
acids through the column and whether unchlorinated phenoxyacetic acid appeared after the chlorinated
acids.   He also asked how long a complete determination of isomers took, and whether ethers other than
ethyl ether, for example, *iso*propyl ether, had been used in this type of chromatographic estimation.

Mr. Stroud said that, although no systematic study of the behaviour of phenol and chlorinated phenols had been made, it was possible to predict from the respective dissociation constants and partition coefficients that phenol and its chlorinated derivatives would run ahead of the chlorinated phenoxyacetic acids. However, these compounds did not interfere with the determinations as they were not titrated under the conditions used. Unchlorinated phenoxyacetic acid appeared after the 2-chlorophenoxyacetic acid and therefore did not interfere.

The complete determination of the isomers could be carried out in half-an-hour to an hour, though the time per determination could be reduced if several determinations were carried out simultaneously.

Other ethers and also other immiscible solvents could be used, although ethyl ether was preferred as it gave a good rate of flow through the column and was readily available. A further advantage was its easy removal by distillation when the acid in a fraction is to be isolated.

Determination of 2-Methyl-4-Chlorophenoxyacetic Acid in Presence of 2-Methyl-6-Chloro- and 2-Methyl-4:6-Dichlorophenoxyacetic Acids by Ultra-Violet Spectrophotometry

By R. HILL

A method is described for the determination of 2-methyl-4-chlorophenoxyacetic acid in presence of 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxyacetic acids by measurement of their ultra-violet absorption. The method is based on that given by Morton and Stubbs for the analysis of vitamin-A oils and depends upon the fact that the absorption due to 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxyacetic acids is approximately linear over the wavelength range 275 to 285 mμ, while 2-methyl-4-chlorophenoxyacetic acid exhibits a peak absorption at 279 mμ. It involves measurements of the extinctions of a solution of the acids in methanol at 275, 279 and 285 mμ, from which the corrected extinction at 279 mμ is obtained and thence the 2-methyl-4-chlorophenoxyacetic acid content of the mixture.

For synthetic mixtures, the accuracy has been found to be 5 per cent. or better.

Since the discovery in 1941 by Slade, Templeman and Sexton[1] of the selective weed-killing activity of 2-methyl-4-chlorophenoxyacetic acid, extensive use has been made of preparations containing this acid. Such preparations are usually aqueous solutions of the sodium salt of 2-methyl-4-chlorophenoxyacetic acid, which, as a consequence of the method of manufacture, contain in addition the sodium salts of 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxyacetic acids, together with sodium chlorocresylate, sodium glycollate and sodium chloride in small amounts.

Extraction of the mixed methyl-chlorophenoxyacetic acids from the remainder of the material can be readily achieved, but there is as yet no published chemical method for the analysis of the extracted mixture of acids. Sjöberg[2] has published an infra-red spectrophotometric method for the analysis of such mixtures and Grabe[3] a method for the determination of 2-methyl-4-chlorophenoxyacetic acid in mixtures with other methyl-chlorophenoxyacetic acids by ultra-violet spectrophotometry. The latter method takes advantage of the fact that, of the methyl-chlorophenoxyacetic acids likely to be present, only 2-methyl-4-chlorophenoxyacetic acid absorbs strongly at 287 mμ. In this laboratory, however, it has been found that this method is not altogether suitable for application to commercial products owing to the presence of impurities that absorb in the region of 287 mμ.

An alternative ultra-violet method, based on that used by Morton and Stubbs[4] for the determination of vitamin A in oils, has been found to be applicable to a large number of commercial samples containing 2-methyl-4-chlorophenoxyacetic acid as the active constituent. The Morton - Stubbs method requires the accurate measurement of the intensities of the total absorption of a mixture at three suitably chosen wavelengths, sufficiently close together to

permit the assumption that the irrelevant absorption, *i.e.*, that part of the total absorption due to unwanted components, is linear over the wavelength range.   If this assumption can be made, then from a consideration of the geometry of the problem it can be shown that—

$$E_{\lambda_1} \text{ (corrected)} = \frac{E_1 k_1 k_2 (\lambda_3 - \lambda_2) - E_2 k_1 k_2 (\lambda_3 - \lambda_1) - E_3 k_1 k_2 (\lambda_1 - \lambda_2)}{k_1 (\lambda_2 - \lambda_1) + k_1 k_2 (\lambda_3 - \lambda_2) + k_2 (\lambda_1 - \lambda_3)} \quad \cdots \quad \cdots \quad (1)$$

where E_1, E_2 and E_3 are the observed extinctions (expressed as log I_o/I) at wavelengths λ_1, λ_2 and λ_3 respectively and k_1 and k_2 are defined by the ratios $E_{\lambda_1}/E_{\lambda_2}$ and $E_{\lambda_1}/E_{\lambda_3}$ for the pure component that it is desired to estimate.   When the wavelengths can be so chosen that $k_1 = k_2 = k$, *i.e.*, when $E_{\lambda_2} = E_{\lambda_3}$, equation (1) reduces to the form—

$$E_{\lambda_1} \text{ (corrected)} = k \left[\frac{E_1 (\lambda_3 - \lambda_2) - E_2 (\lambda_3 - \lambda_1) - E_3 (\lambda_1 - \lambda_2)}{(\lambda_2 - \lambda_1) + k(\lambda_3 - \lambda_2) + (\lambda_1 - \lambda_3)} \right] \quad \cdots \quad \cdots \quad \cdots \quad (2)$$

EXPERIMENTAL

DETERMINATION OF ABSORPTION SPECTRA—

The ultra-violet absorption spectra of 2-methyl-4-chloro-, 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxyacetic acids were determined for 0·01 per cent. w/v solutions of the acids in AnalaR methanol with quartz cells of path length 1 cm and a Hilger "Uvispek" spectrophotometer (Fig. 1).
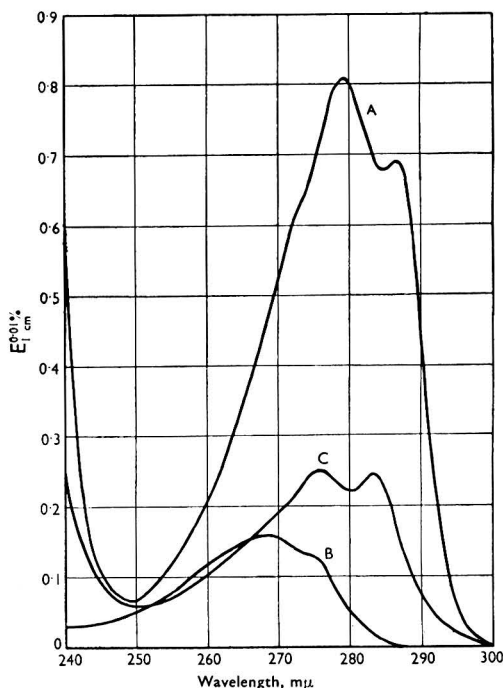
Fig. 1.   The ultra-violet absorption spectra of (A) 2-methyl-4-chlorophenoxy-acetic acid, m.p. 120° C, (B) 2-methyl-6-chloro-phenoxyacetic acid, m.p. 110° C, and (C)   2-methyl-4 : 6-dichlorophenoxyacetic acid, m.p. 184° C

From a study of these spectra it was considered that by using the wavelengths 275, 279 and 285 mμ, the Morton - Stubbs method could be applied and equation (2) used, since (*a*) the extinction coefficients of both 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxy-acetic acids are small at these wavelengths, compared with the 2-methyl-4-chloro-isomer and

(b) the extinction values for 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxyacetic acids at 275, 279 and 285 mμ lie approximately on straight lines.

By substituting $\lambda_1 = 279$ mμ, $\lambda_2 = 275$ mμ and $\lambda_3 = 285$ mμ in equation (2), the following expression was obtained—

$$E_{279} \text{ (corrected)} = \frac{k}{k-1} [E_{279} \text{ (obs.)} - 0\cdot6E_{275} \text{ (obs.)} - 0\cdot4E_{285} \text{ (obs.)}] \quad .. \qquad .. \qquad (3)$$

where $k = E_{279}/E_{285} = E_{279}/E_{275}$ for pure 2-methyl-4-chlorophenoxyacetic acid.

VALIDITY OF BEER'S LAW AND EVALUATION OF k—

The extinctions of a number of solutions of 2-methyl-4-chlorophenoxyacetic acid, of various concentrations from 0·004 to 0·02 per cent., were measured at 275, 279 and 285 mμ with 1-cm cells (Table I) and plots of extinction against concentration were made from which it was deduced that Beer's law holds up to a concentration of 0·016 per cent., but for higher concentrations there was a slight falling off from linearity.

The value of the constant k was determined by taking the average of the values for E_{279}/E_{285} for concentrations of 2-methyl-4-chlorophenoxyacetic acid of 0·004, 0·008, 0·010 and 0·016 per cent. (Table I). Substitution for k ($= 1\cdot1914$) in equation (3) gave the following expression—

$$E_{279} \text{ (corrected)} = 6\cdot224 [E_{279} \text{ (obs.)} - 0\cdot6E_{275} \text{ (obs.)} - 0\cdot4E_{285} \text{ (obs.)}] \quad .. \qquad .. \qquad (4)$$

TABLE I

VALIDITY OF BEER'S LAW AND THE EVALUATION OF k

Conc. of soln., % w/v	$E_{275m\mu}$	$E_{279m\mu}$	$E_{285m\mu}$	k = E_{279}/E_{285}
0·004	0·265	0·319	0·267	1·1963
0·008	0·543	0·648	0·544	1·1912
0·010	0·676	0·802	0·674	1·1900
0·016	1·063	1·267	1·057	1·1872
0·020	1·334	1·580	1·322	—

Average value of k = 1·1914.

APPLICATION OF EQUATION (4) TO SYNTHETIC MIXTURES—

Six mixtures containing known amounts of 2-methyl-4-chloro-, 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxyacetic acids were examined with the results shown in Table II. These results were obtained by taking 0·01 per cent. w/v solutions of each mixture, measuring the extinctions in 1-cm cells at 275, 279 and 285 mμ and calculating the corrected extinctions at 279 mμ, from which the 2-methyl-4-chlorophenoxyacetic acid contents were computed.

Replicate determinations on each sample gave results which were satisfactorily reproducible.

TABLE II

APPLICATION OF EQUATION (4) TO SYNTHETIC MIXTURES

Mixture	Composition, %			2-Methyl-4-chloro-acid found, %	
	2Me-4Cl	2Me-6Cl	2Me-4:6-Cl	Individual values	Average
1	95	2	3	92, 94, 95	94
2	85	3	12	84, 86, 85	85
3	80	15	5	80, 79, 79	79
4	71	26	3	72, 71, 73	72
5	62	30	8	63, 62, 63	63
6	49	36	15	48, 48, 47	48

METHOD

The following procedure was adopted for commercial preparations containing sodium 2-methyl-4-chlorophenoxyacetate in aqueous solution.

REAGENTS—

Hydrochloric acid, 5 *N*.
Chloroform—A.R. or B.P.
Sodium bicarbonate—A half-saturated aqueous solution.
Methyl alcohol—AnalaR.

PROCEDURE—

Take sufficient of the sample to give 0·5 to 1·0 g of mixed methyl-chlorophenoxyacetic acids, dilute to 50 ml in a separating funnel and make distinctly acid with hydrochloric acid. Extract three times with portions of chloroform and combine the chloroform extracts. Extract the chloroform layer three times with half-saturated sodium bicarbonate solution to obtain the acids free from chlorocresols and combine the extracts. Acidify with hydro-chloric acid and extract the liberated acids three times with chloroform. Run the chloroform extracts into a small flask and dry by addition of 1 to 2 g of anhydrous sodium sulphate. After a few minutes pour off the chloroform into a beaker, washing the sodium sulphate with small amounts of chloroform. Evaporate the chloroform and dry the residue of methyl-chlorophenoxyacetic acids on a steam-bath for exactly 10 minutes after removal of the solvent.

Weigh out accurately 100 ± 0·5 mg of the extracted acids and dissolve in methanol, making up the volume of solution to 100 ml in a standard flask. Pipette 10 ml of this solution into a second 100-ml standard flask and dilute to the mark with methanol to give a 0·01 per cent. w/v solution of the acids. With a photo-electric spectrophotometer, measure the extinctions of this solution at 275, 279 and 285 mμ in a 1-cm cell, using methanol from the same batch as is used to prepare the solutions in the "blank" cell.

With the extinction values so obtained, use equation (4) to calculate—

$$E_{279} \text{ (corrected)} = 6 \cdot 224 \left[E_{279} \text{ (obs.)} - 0 \cdot 6 E_{275} \text{ (obs.)} - 0 \cdot 4 E_{285} \text{ (obs.)} \right]$$

and read the 2-methyl-4-chlorophenoxyacetic acid content from a previously prepared calibration curve.

CONCLUSIONS

The results of tests on synthetic mixtures indicate that the method is reliable for samples of mixed acids containing 50 per cent. or more of 2-methyl-4-chlorophenoxyacetic with 2-methyl-6-chloro- and 2-methyl-4:6-dichlorophenoxyacetic acids as the only other major constituents.

The chief advantage of this method is speed, it being possible to analyse in duplicate three samples of extracted acids in less than 2 hours.

The disadvantages of the method are (*a*) the relatively large values of the constants in equation (4), which means that great care must be taken in the determination of extinction values, and (*b*) probability of interference from 2-methyl-phenoxyacetic acid, which has an absorption maximum at 277 mμ. However, it does not appear that, in general, the proportion of this acid will exceed 5 per cent. of the total acids in the sample, in which circumstances the accuracy of the result will not be appreciably affected.

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The Determination of *o*-Tolyl Ester in Tritolyl Phosphate

BY J. HASLAM AND D. C. M. SQUIRRELL

A method has been devised for the determination of the *o*-tolyl ester in commercial tritolyl phosphate. The test, which is based on previous work carried out by Wurzschmitt, involves the preliminary isolation of the mixed cresols from the ester, followed by condensation of these cresols with benzaldehyde in a sulphuric acid medium. On being made alkaline the product obtained from *o*-cresol under these conditions yields a coloured solution, which is examined absorptiometrically. The method is suitable for the determination of up to 6 per cent. of *o*-tolyl ester in commercial tritolyl phosphate, without modification, and of a corresponding amount of *o*-cresol in mixed cresols. The influence of phenol and various xylenols on the test has been investigated.

CONSIDERABLE interest has been taken recently in this country in the proportion of *o*-tolyl esters in commercial samples of tritolyl phosphate. The reason for this is that there appears to be no doubt that tri-*o*-tolyl phosphate is a dangerously toxic material. There is a voluminous literature on the subject and Blomqvist[1] has summarised the position as follows—

"Cresol is a mixture of three isomers. Of the esters with phosphoric acid the *m*- and *p*-isomers are innocuous, but tri-*o*-cresyl phosphate is a dangerously toxic material. It attacks the central nervous system, causing paralysis of the extremities. As little as 0·15 to 0·3 g produces the characteristic symptoms. Poisoning has mainly occurred by consumption of the substance, but some German cases are reported where paralysis has been caused by vinyl sheet plasticised with tricresyl phosphate containing a high proportion of the *o*-isomer. Tri-*o*-cresyl phosphate in liquid form being absorbed through skin, it is advisable to specify not more than 3 per cent. of *o*-isomer in tricresyl phosphate for use in vinyl plastics. Experience has shown no hazards need be anticipated then."

Certain authorities have taken steps to restrict the proportion of *o*-tolyl ester in tritolyl phosphate. For example, in the Eastern Zone of Germany a limit of 6 per cent. has been set[2] and in Sweden a limit of 3 per cent. has been advised by Blomqvist.[1] It is understood that a limit of 3 per cent. is being contemplated in America.

Apparently most of the work on toxicity has been concerned with the dangerous character of the tri-*o*-tolyl ester, so although it may be possible at a later date to obtain more precise information about the relative toxicities of tritolyl phosphates of mixed *o*-, *m*- and *p*-esters, it seems desirable at the present time to limit the proportion of *o*-cresol in the mixed cresols used in the preparation of the tritolyl ester, as this will at least limit the proportion of tri-*o*-tolyl ester that can possibly be present in a commercial product. We do not doubt that if the demand arises, it will be possible, at a later date, possibly by infra-red methods, to determine the relative proportions of mixed tolyl esters in the commercial products.

The purpose of this paper, therefore, is to describe the methods that we have found to be most useful in the determination of (*a*) *o*-cresol in mixed cresols and (*b*) the *o*-tolyl radicle in commercial samples of tritolyl phosphate. This work is based on previous work of Wurzschmitt,[3] who showed that *o*-cresol, when heated with freshly distilled benzaldehyde in the presence of 75 per cent. sulphuric acid, produced a benzein dyestuff of the formula—
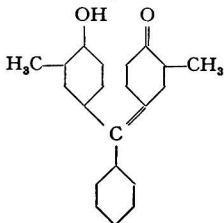
This dyestuff is red in acid solution and blue - violet in alkaline solution. Under corresponding conditions *m*- and *p*-cresol do not give coloured products. In our hands Wurzschmitt's method failed in several respects and we have had to modify his test in at least five important particulars, as follows:

Method of extraction and purification of the mixed cresols from the hydrolysis products of tritolyl phosphate—After the hydrolysis of the tritolyl phosphate we find it necessary to extract with ether, first on the alkaline side in order to remove interfering substances, then on the acid side in order to extract the resulting cresols. The residue of cresols obtained on removal of the ether solvent is not a satisfactory product for benzaldehyde condensation and requires purification by distillation.

Conditions of temperature, time, acid concentration and so on used in the condensation with benzaldehyde—These conditions must be well defined and strictly adhered to in order to obtain a resinous condensation product that is completely soluble in methanol.

Extraction and purification of the condensation product and its subsequent solution—After careful washing, the condensation product contains a small amount of sulphuric acid that in its turn produces a small amount of sodium sulphate when made alkaline in the colorimetric test. It is necessary to pay strict attention to the ratio of methyl alcohol to water used at this stage of the procedure in order that any traces of sodium sulphate produced do not interfere in the colorimetry.

Method of preparation of standards—In Wurzschmitt's paper but little attention was paid to the preparation of standards. In our work, the colour standards have been prepared from known amounts of *o*-cresol mixed with a known amount of *m*- and *p*-cresols, free from *o*-cresol.

Use of the Spekker absorptiometer and Lovibond colour disc in the final colour comparison—Wurzschmitt gives no detailed information about the method used to effect colour comparison of the *o*-cresol - benzaldehyde condensation product. In the method that we normally use the final colour comparison is made with a Spekker absorptiometer, the range covered being from 0 to 12 mg of *o*-cresol per 50 ml of coloured solution. With the co-operation of The Tintometer Ltd., two colour discs have been prepared to cover the range 0 to 12 mg of *o*-cresol per 50 ml of coloured solution in 13 steps, and it is suggested that these discs may be of value in the day-to-day control of the quality of mixed cresols used for the preparation of tritolyl phosphate.

The observations of Mr. G. J. Chamberlin of The Tintometer Ltd. on the colours obtained may be of interest. In his view, with low concentrations of *o*-cresol the colour obtained is predominantly yellow. With increasing amounts of *o*-cresol the colour then changes through a greenish grey to a dirty mauve. This appears to be a dichroic solution with two absorption bands that change in relative importance as the concentration increases.

The method that we have evolved for the determination of the proportion of *o*-tolyl esters in tritolyl phosphate is given below. It should be remembered that it is the *o*-cresol content of the mixed cresols recovered from the tritolyl phosphate that is determined, and it is inferred that this figure is precisely the same as the calculated proportion of the tri-*o*-tolyl ester in the original tritolyl phosphate under test.

METHOD

REAGENTS—

Cellosolve potash, 50 *per cent. w/v*—Dissolve 12·5 g of potassium hydroxide pellets in 25 ml of ethylene glycol mono-ethyl ether by heating under reflux for 5 minutes in the hydrolysis flask.

Sulphuric acid—Diluted (1 + 1) and 75 per cent. v/v.

Ether.

Sodium sulphate—Anhydrous.

Benzaldehyde—Redistil AnalaR grade.

Ammonium hydroxide, 0·5 *per cent. w/v*—Dilute 20·5 ml of ammonium hydroxide, sp.gr. 0·880, with water to 1 litre.

Methyl alcohol.

Sodium hydroxide, 10 *per cent. w/v*.

PROCEDURE FOR THE HYDROLYSIS OF THE TRITOLYL PHOSPHATE AND EXTRACTION OF THE RESULTING CRESOLS—

Heat 4 g of the sample with 25 ml of Cellosolve potash under reflux for $2\frac{1}{2}$ hours. Cool the solution and dilute with 150 ml of distilled water, and then extract successively with two 25-ml portions of ether; discard the extracts. Acidify the aqueous layer by the dropwise addition of diluted sulphuric acid (1 + 1) with cooling and extract the acid solution successively with two 25-ml portions of ether; wash the combined ether extracts twice with 50-ml portions of distilled water and dry over anhydrous sodium sulphate before evaporation of the bulk of the ether on a water-bath. Transfer the residual cresols to a small (10-ml) distillation flask and distil. After the preliminary removal of the remaining ether, collect the fraction distilling to the dry point.

PROCEDURE FOR CONDENSATION WITH BENZALDEHYDE—

Transfer 14 drops (about 0·3 g) of the mixed cresols to the bottom of a 6-inch by $\frac{1}{2}$-inch hard-glass test tube. Weigh the test tube before and after the addition of the cresols. Add 14 drops of redistilled benzaldehyde and mix thoroughly with the weighed amount of mixed cresols. Immerse the tube and contents to a depth of 2 inches in an oil-bath maintained at 130° ± 1° C. After half a minute, add 5 ml of 75 per cent. v/v sulphuric acid dropwise over a period of 1 minute, with constant stirring by means of a glass rod. Allow the test tube and contents to remain in the oil-bath for a further minute; *i.e.*, the total time of immersion should be $2\frac{1}{2}$ minutes.

After cooling for 20 minutes dilute the mixture with 10 ml of distilled water and filter through a compressed cotton-wool pad in a small porcelain Gooch crucible, 3·5 cm by 2 cm, suction being applied by means of a water pump. With a glass rod, thoroughly break up the insoluble residue on the pad and wash it carefully with at least 100 ml of cold water. This operation is very important, as it is desirable to remove occluded sulphuric acid at this stage. Wash the resin with 40 ml of water at 50° to 60° C, then with 2 ml of 0·5 per cent. w/v ammonium hydroxide and finally with cold water.

Transfer the crucible and contents to a flat-bottomed flask, of 100-ml capacity and with a 3-cm neck, and heat under reflux for 10 minutes with 15 ml of methanol to dissolve the resin. Filter the solution of the resin through a 3-cm Whatman No. 1 filter-paper supported by a filter disc contained in a funnel over a side-arm boiling-tube graduated at 30 ml. Wash the flask and crucible with methanol until the volume of the filtrate is 30 ml.

COLORIMETRY—

Transfer 20 ml of this methanol solution, by means of a pipette, to a 50-ml standard flask. Add 0·5 ml of 10 per cent. w/v sodium hydroxide solution and 12 ml of distilled water. Mix and dilute the solution to the mark with methanol. Filter this solution through a Whatman No. 42 filter-paper into a 1-cm cell and measure the colour in a Spekker absorptiometer 15 minutes after making alkaline and diluting to the mark. Use spectrum yellow filters, No. 606, and Calorex heat absorbers. For the blank use a 75 per cent. v/v solution of methanol in water.

From mixtures made by adding known weights of *o*-cresol to a 50 per cent. w/w mixture of *m*- and *p*-cresol, prepare by the above procedure a calibration curve to cover the range 0 to 12 mg of *o*-cresol per 50 ml of final coloured solution, *i.e.*, from 0 to 6 per cent. of *o*-cresol on a 0·3 g sample. From this curve or from the appropriate Lovibond disc deduce the *o*-cresol content of the unknown cresol mixture. Should the cresols contain more than 6 per cent. of *o*-cresol, a proportionately smaller sample should be taken and diluted to approximately 0·3 g with the 50 per cent. w/w mixture of *m*- and *p*-cresol before the condensation with benzaldehyde. The percentage of *o*-cresol found is assumed to be equivalent to the tri-*o*-tolyl phosphate content of the tritolyl phosphate originally submitted to test.

A typical calibration curve is a straight line passing through the following points—

Indicator drum reading	0·002	0·058	0·115	0·170	0·226	0·284	0·340
o-Cresol corresponding to 50 ml of coloured solution, mg	0	2	4	6	8	10	12

NOTES

In the course of the work certain other conclusions have been reached and they may be of interest.

Efficiency of hydrolysis—It has been shown that the hydrolysis of the tritolyl phosphate with Cellosolve potash is very efficient. In given experiments less than 0·2 per cent. of the tritolyl phosphate remained unhydrolysed at the conclusion of the operation.

Interference of phenol and xylenols—The interference of phenol and 2:3-, 2:4-, 2:5-, 2:6-, 3:4- and 3:5-xylenols in the test has been investigated. We are indebted to Mr. P. J. C. Haywood for the supply of authentic samples of these xylenols. There is no interference from 2:3-, 2:4-, 2:5-, 3:4- and 3:5-xylenols, but 2:6-xylenol and phenol do interfere in the test. The magnitude of the interference is demonstrated by the fact that 3 per cent. of phenol would be reported as 1·8 per cent. of *o*-cresol and 3 per cent. of 2:6-xylenol would be reported as 3·6 per cent. of *o*-cresol if examined as unknown samples. In the examination of commercial material it is unlikely that this interference would prove to be serious, as we understand that the maximum 2:6-xylenol content of commercial cresylic acid is of the order of 0·3 per cent. and the maximum phenol content is of the order of 1 per cent.

Flasks—The hydrolysis with Cellosolve potash proceeds smoothly in soda-glass flasks and the life of these flasks is satisfactory. In contrast, Pyrex flasks do not withstand the conditions of the test and should not be used.

Stability of colour—The condensation product is not stable if allowed to stand for a long time in methanol solution, so the colorimetry should be completed within 3 hours of dissolving the resin in methanol. Throughout the test the same time intervals should be used for the samples as are used in the preparation of the standard colour.

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The Determination of Water in Liquid Ammonia

By H. W. HODGSON and J. H. GLOVER

A method is described for the determination of water in liquid ammonia. The ammonia is removed by evaporation after addition of ethylene glycol to retain the water. The water is titrated with Fischer reagent after neutralisation of traces of residual ammonia with acetic acid. Results are given to show the advantage of the method over that of direct evaporation with no water retaining agent; the accuracy and reproducibility are also shown.

A METHOD for the determination of water in liquid ammonia was described by Iljin and his co-workers.[1] Liquid ammonia was allowed to evaporate from a Dewar flask through weighed absorption tubes containing sodium hydroxide pellets; the water content was calculated from the increase in weight of the absorption tubes and the weight of ammonia lost from the Dewar flask. There is no evidence to support the assumption that water is carried over quantitatively with the ammonia in this method.

Pleskov[2] described a method that depended on the blue colour of a solution of sodium in liquid ammonia. He added a weighed amount of sodium to a known volume of liquid ammonia and titrated the solution with more liquid ammonia until the blue colour was discharged. Experiments were carried out by Pleskov's method, but it was found that the amount of sodium required to produce a permanent blue colour was much more than could be accounted for by the known water content of the sample.

According to Mitchell and Smith[3] the water in liquid ammonia can be determined by Fischer reagent after the addition of methanol and the subsequent removal of ammonia by vacuum distillation. The method is not described in detail and the result quoted is cited from unpublished work.

SAMPLING OF LIQUID AMMONIA METHOD—

The low boiling-point and the hygroscopic nature of liquid ammonia necessitated the development of a special technique for sampling and storing the material. The sample is taken in a small steel cylinder, of about 2 litres capacity, fitted with a needle valve at each end. The cylinder is dried by rinsing with acetone and blowing through with compressed air. The dry sampling cylinder is connected by an adaptor and flexible metal tube to the source of liquid ammonia, and, with both valves open, ammonia is blown through until the temperature has dropped sufficiently for liquid ammonia to issue from the bottom valve. This valve is then closed, the sampling cylinder is left in position for five minutes, the other valve is closed and the cylinder disconnected.

APPARATUS—

The apparatus is illustrated in Fig. 1; the tube, A, is graduated with one mark at 12 ml and constructed from a 6 × 1-inch Pyrex boiling tube fitted with a standard ground joint
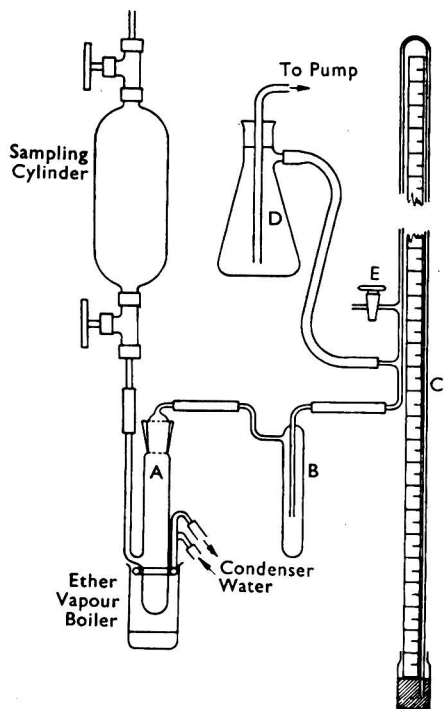
Fig. 1.   Evaporation assembly
A, titration tube; B and D, traps; C, mercury gauge; E, stopcock to give controlled variable leak

Fig. 2.   Titration assembly

and carrying a side-arm that joins the main tube just above the graduation mark. The tube, A, is connected by a standard cone to the trap, B, and thence through the mercury gauge, C, to the trap, D, and finally to the water pump. A controlled variable leak is provided by the stop-cock, E.

PROCEDURE—

Attach the sampling cylinder to the side-arm of the tube, A, by a short length of pressure tubing. Immerse the trap, B, in a bath containing acetone and solid carbon dioxide at −78° C, and reduce the pressure in the system to about 40 mm of mercury for ten minutes so that traces of water in the tube, A, and its connections are transferred to the trap, B. Restore to atmospheric pressure by opening the stop-cock, E. Place 2 ml of ethylene glycol,

containing less than 0·1 per cent. of water, in the tube, A, by means of a pipette, replace the connecting cone, and immerse the tube and its contents in another bath containing acetone and solid carbon dioxide at −78° C.

Cautiously open the valve on the sampling cylinder, so that liquid ammonia is run into the tube, A, via the side-arm. The side-arm acts as a short condenser and prevents loss of ammonia as gas. Close the valve as soon as the liquid level reaches the graduation mark. Remove the cooling bath from around the tube A, wipe the outside of the tube and immerse the bottom part of the tube in the ether vapour boiler.

The boiler, a 100-ml beaker containing ether, is heated by a small electric hot-plate. The condensing ether supplies enough heat to the ammonia to maintain steady boiling.

Reduce the pressure to about 650 mm, so that the ammonia gas not condensed in the trap, B, is removed by the water pump. When the bulk of the ammonia has evaporated, further reduce the pressure to 150 mm, continue to heat with the ether vapour bath and introduce a single-coil copper condenser around the tube, A, to prevent loss of ether. After 15 minutes, restore to atmospheric pressure and disconnect the tube, A, from the trap, B.

Take 10 ml of a 10 per cent. solution of acetic acid in methanol, and titrate with Fischer reagent. Add about 10 ml of the titrated solution to the residue in the tube, A, immediately after disconnecting, and attach the tube to the titration apparatus, Fig. 2. Titrate the water in the sample and glycol (T_1) with Fischer reagent, then add 2 ml of the glycol with the original pipette and titrate to determine the glycol blank (T_2).

$$\text{Water, \% w/v} = (T_1 - T_2) \times 10 \times \text{W.E.}$$

where W.E. is the water equivalent of the Fischer reagent.

DISCUSSION

Preliminary experiments indicated that ammonia interferes seriously with titrations with Fischer reagent, and early work was directed towards neutralising the ammonia before titration. Various methanolic solutions of acids were tried, but it was found that no satisfactory method could be developed with this procedure; the large amounts of reagents needed to neutralise 10 ml of liquid ammonia gave rise to manipulative difficulties, and heavy precipitates were formed.

Spontaneous evaporation of 50 ml of liquid ammonia and titration of the residual water with Fischer reagent gave low and erratic results, which were only useful as an indication of the water content.

Experiments were made to determine the effectiveness of separation of liquid ammonia from water by evaporation. Known weights of water were added to liquid ammonia in the tube, A, the ammonia was evaporated under the conditions of the method and the residual water determined by titration with Fischer reagent. Results are shown in Table I.

TABLE I

SEPARATION OF LIQUID AMMONIA FROM WATER BY DIRECT EVAPORATION

Liquid ammonia taken, ml	Water taken, g	Water found, g	Recovery of water, %
10	0·050	0·049	98
10	0·100	0·101	101
10	0·100	0·098	98
10	0·200	0·180	90
10	0·250	0·213	85
10	0·300	0·260	87
10	0·500	0·276	55

These results showed that loss of water is significant if more than 1 per cent. is present in the sample. Although most samples of liquid ammonia would be expected to contain less than 1 per cent. of water, it was necessary to extend the method to samples containing water in excess of this amount. Loss of water was prevented by the use of a high-boiling hygroscopic liquid as a retaining agent. The effect of using ethylene glycol was demonstrated by a series of tests in which mixtures of glycol and water were subjected to conditions similar to those of the determination. Table II shows results obtained in this way. The accuracy

TABLE II

ETHYLENE GLYCOL AS A WATER RETAINING AGENT

Liquid ammonia taken, ml	Ethylene glycol taken, ml	Water added, g	Water found, g	Recover of water, %
nil	nil	0·047	0·031	65
nil	2	0·705	0·702	99
nil	2	0·191	0·190	99
10	2	0·300	0·291	97
10	2	0·086	0·087	101

of the method has been examined by analysing a series of synthetic mixtures prepared by adding anhydrous ammonia to weighed amounts of water in glycol. The results for the synthetic mixtures are shown in the first part of Table III; the second part shows results of replicate analyses of samples derived from commercial sources. The trap shown in

TABLE III

ACCURACY AND REPRODUCIBILITY

Synthetic mixtures—

Water added, %	Water found, %	Water added, %	Water found, %
0·86	0·87	0·23	0·23
0·64	0·64	0·21	0·19
0·71	0·68	0·09	0·12
0·88	0·84	0·08	0·09
0·48	0·49	0·06	0·07
0·41	0·44	0·05	0·03
0·41	0·42	0·01	0·02
0·34	0·30		

Commercial samples—

Water found, %		Water found, %		
0·04,	0·04	0·07,	0·08	
0·07,	0·08	0·09,	0·09	
0·01,	0·01	0·11,	0·12,	0·09

Fig. 1 has proved to be the most efficient type for preventing water vapour from entering the apparatus from the pump. As the determination proceeds, ammonia condenses in the trap, and this, together with the low temperature, prevents any passage of moisture to the sample.

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Inorganic Chromatography on Cellulose

Part VII

The Determination of Thorium in Monazite and of Thorium and Uranium in Uranothorianite

By N. F. KEMBER

A method is described for the quantitative separation of thorium from other metals; it is based on the extraction of thorium nitrate with ether containing nitric acid on a column of cellulose. The method has been applied to the determination of thorium in monazite sands and, by means of a double extraction technique, uranium and thorium have been determined on the same sample of uranothorianite. The behaviour of a number of other anions and cations has been investigated.

ALTHOUGH the solubility of thorium nitrate in organic solvents has been widely observed,[1] this factor has not been used previously for the determination of thorium. The successful use of organic solvents in conjunction with columns of cellulose absorbent for the determination of various metals suggested that a similar procedure could be developed for the determination of thorium. The separation of thorium nitrate from a number of other metals on a paper strip with tetrahydrosylvan containing nitric acid has already been recorded.[2] It was observed during work with cellulose columns on the analysis of uranium products[3] and in preliminary work by T. V. Arden of this laboratory, that thorium nitrate was partly extracted by solvents consisting of ethyl ether containing small amounts of nitric acid. By increasing the concentration of nitric acid, sp.gr. 1·42, to 12·5 per cent. v/v it was possible to extract thorium nitrate quantitatively, and this observation has been made the basis of a method for the determination of thorium in minerals and ores. The values obtained by this procedure show greater consistency than those by established procedures, particularly for very crude ores.

The procedure consisted in preparing a nitrate solution of the sample of monazite sand, free from phosphate, and allowing it to percolate through a cellulose column previously prepared in ether containing 12·5 per cent. v/v of nitric acid, sp.gr. 1·42. Thorium nitrate passed quantitatively into the solvent and was extracted, whereas most of the other metals present remained in the column. The thorium nitrate was recovered from the eluate after removal of the solvent by distillation and the thorium precipitated as oxalate, ignited and finally weighed as ThO_2.

The method was also adopted for the analysis of uranothorianite for both uranium and thorium on the same sample. The uranium was extracted with ether containing 3 per cent. v/v of nitric acid, sp.gr. 1·42, which left thorium at the top of the column. When extraction of uranium was complete, the solvent was changed to ether containing 12·5 per cent. v/v of nitric acid, sp.gr. 1·42, and the thorium was extracted.

Under the conditions used for the extraction of thorium, scandium and zirconium were extracted, although more slowly and less completely than thorium. The movement of these metals was prevented by addition of tartaric acid to the original nitrate solution.

The theoretical considerations controlling the efficiency of the separation are similar to those already recorded for uranium.[3]

EXPERIMENTAL

EXTRACTION OF THORIUM NITRATE—

Preliminary experiments were carried out in order to ascertain the lowest concentration of nitric acid in the ether and the volume of solvent needed to extract the thorium nitrate quantitatively. The original solution contained 0·4706 g of thorium dioxide in each 5 ml of 6 N nitric acid and the extractions were carried out in 25-cm columns of cellulose, the

eluate being collected in three fractions of 150 ml each.   The results in Table I show that the best acidity was 12·5 per cent., no advantage being gained at higher acidity.

TABLE I

EFFECT OF ACIDITY OF THE SOLVENT ON THE EXTRACTION OF THORIUM NITRATE

Nitric acid in solvent, %	Thorium nitrate (expressed as ThO₂) in						Total, %
	First 150 ml,		Second 150 ml,		Third 150 ml,		
	mg	%	mg	%	mg	%	
3	<0·05	<0·01	<0·05	<0·01	20·54	4·37	4·37
5	0·25	0·05	0·30	0·06	39·30	8·36	8·47
7·5	5·95	1·26	11·48	2·44	240·2	51·06	54·76
10	227·3	48·3	160·0	34·0	17·85	3·80	86·1
12·5	398·0	84·5	34·06	7·2	6·67	1·41	93·1
15	400·1	85·0	34·19	7·3	5·12	1·09	93·3

In order to ascertain the volume of solvent needed to give complete extraction at this acidity a further experiment was carried out in which a larger volume of solvent was used. Only 0·05 mg of thorium dioxide was detected between 700 and 800 ml and none after that, 99·5 per cent. of the original weight of thorium dioxide being recovered from the eluates. In an attempt to reduce the volume of solvent needed, the effect of shortening the column was tested, but gave no advantage.   It was apparent that the large volume of solvent needed was not caused by adsorption on the cellulose, but by the low solubility or partition of the thorium nitrate in the solvent.   A number of extractions were carried out with various quantities of thorium nitrate and 400 ml of solvent.   The results in Table II show that complete extraction of 0·25 g of thorium dioxide was achieved, but larger amounts were not completely extracted.

TABLE II

EFFECT OF INCREASE IN AMOUNT OF THORIUM NITRATE IN ORIGINAL SOLUTION

ThO₂ present, g	ThO₂ extracted in 400 ml, g	ThO₂ extracted, %
0·2481	0·2481	100·0
0·4706	0·4515	94·8
0·9412	0·8661	92·0
1·8824	1·6720	88·8

In the analyses carried out at a later stage, 600 ml of solvent were used.   This increase was necessary to compensate for the increase in the volume of the original solution, as it was found that the rate of extraction of thorium nitrate decreased with an increase in the volume of water in the original solution.

Since monazite sands contain a large proportion of phosphate, the effect of phosphate ions on the extraction of thorium nitrate is important.   A number of experiments were carried out to investigate the effect of addition of phosphoric acid when ether containing 12·5 per cent. of nitric acid was used as solvent.   After the addition of one equivalent of phosphoric acid to a known amount of thorium nitrate, 48 per cent. of the thorium was recovered after the passage of 300 ml of solvent, and after the addition of 0·1 equivalent, 94 per cent. was recovered; this demonstrated the necessity of removing phosphates.   The addition of sulphate or oxalate to the solution also led to low results.

MOVEMENT OF METALS OTHER THAN THORIUM

As the final estimation of thorium was carried out by precipitation with oxalic acid, a study was made of those metals that precipitated or tended to co-precipitate under these conditions.   The nitrates of Ca, Sn, Pb, Fe, Co, Ni, Cu and Ti did not move more than 2 cm down the column.   The remaining nitrates of interest moved as described below.

THE RARE EARTHS—

Quadrivalent cerium moved with thorium as a yellow band, but in the cerous form it moved no more than 2 cm; hence it was necessary to reduce all the cerium to its lower valency

form before extraction. With samples containing small amounts of cerium, the reducing powers of the cellulose and solvent were sufficient, but in most samples the cerium content was too high for the reaction to go to completion. Ferrous sulphate was effective as a reducer, but a cleaner and more efficient method was to add a few drops of 20-volume hydrogen peroxide to the sample solution and boil to remove excess of peroxide.

With non-activated cellulose pulp, *i.e.*, pulp made by mechanical disintegration of cellulose in water, some difference in the rate of movement of the rare-earth nitrates was detected, those of higher atomic weight moving faster. Fig. 1 shows the distribution of a
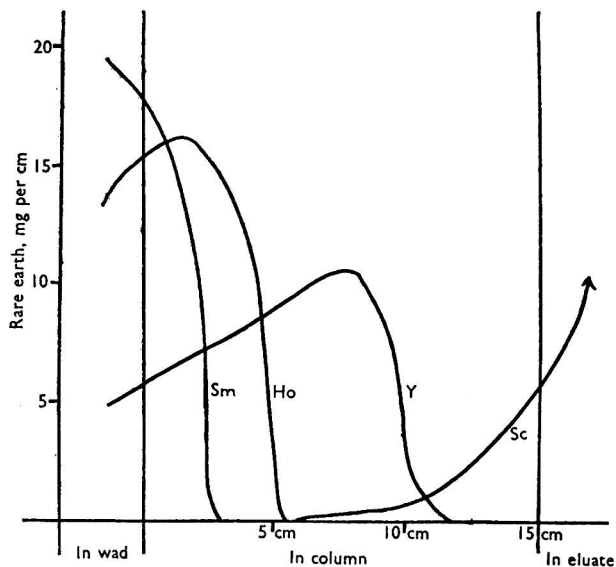
Fig. 1. Movement of rare earths in a column of non-activated cellulose pulp

number of rare earths and pseudo rare earths (scandium and yttrium) in such a column after the passage of 500 ml of solvent. With activated pulp, *i.e.*, pulp made by boiling cellulose with dilute nitric acid, the movement of all the rare earths is reduced, and after the passage of 600 ml of solvent none was detected as having moved more than 3 cm.

YTTRIUM—

The movement of yttrium was shown to be largely dependent on the type of pulp used. No difficulty was found in holding back the yttrium nitrate when activated pulp, *i.e.*, pulp treated with dilute nitric acid, was used, and although yttrium moved down the column more rapidly than any of the true rare earths, none was detected as having moved more than 3 cm after the passage of 600 ml of solvent.

With non-activated pulp, however, partial extraction of yttrium nitrate was observed and a purification was carried out on a sample of commercial quality "yttria," which contained some cerium and a trace of gadolinium. After solution of 0·75 g of the oxide in nitric acid the sample was transferred to a column and extracted with 800 ml of solvent. From the eluate 0·18 g of oxide was recovered and was shown spectrographically to be free from cerium and gadolinium.

SCANDIUM—

It was shown that the extraction of scandium nitrate was almost as rapid as that of thorium nitrate, so that increasing the length of the column gave no advantage. As ammonium tartrate has been used for the partial separation of scandium and thorium, its effect on the chromatographic separation was investigated. In one column it was shown that the addition of up to 3 g of tartaric acid to the nitrate solution did not affect the extraction of thorium; in a second column 0·1 g of Sc_2O_3 as nitrate was added to a known weight of

thorium nitrate and 3 g of tartaric acid.   After extraction with 600 ml of solvent, a quantitative yield of oxide (ThO_2) was recovered from the eluate, whilst the scandium was found to be entirely within the top 10 cm of the column.   On spectrographic analysis the scandium was shown to be completely free from thorium.   Scandium can normally be disregarded when dealing with monazite sands, in which it rarely occurs.

ZIRCONIUM—

Preliminary experiments showed that zirconyl nitrate moved almost as rapidly as thorium nitrate in the column.   As in uranium extraction,[3] the addition of tartaric acid to the original solution was also found to inhibit the movement of zirconium.   Most monazite sands, however, contain not more than 1 per cent. of ZrO_2 and the final oxalate precipitation was sufficient to purify the thorium from zirconium, as zirconium oxalate is soluble in an excess of reagent.

To test the efficiency of the separation of thorium nitrate from other nitrates, a number of extractions of synthetic mixtures was carried out.   The results shown in Table III indicate complete separation in all experiments.   The oxides obtained on ignition of the oxalates were always pure white.

TABLE III

ANALYSIS OF SYNTHETIC MIXTURES CONTAINING THORIUM NITRATE

ThO_2 present, g	Other metals added	ThO_2 found, g	Yield, %
0·4706	1 g of La, 0·1 g of Ce*	0·4737	100·7
0·2481	1 g of La, 0·1 g of Ce	0·2485	100·2
0·1882	0·1 g of Sc†	0·1893	100·6
0·2481	0·1 g each of La, Ce, Fe, Co, Ni, Cu, Ti, Sn, Y, Ca, Yb	0·2489	100·3

* 800 ml of solvent used.   † Tartaric acid added to original solution.

It was shown in Table I that no thorium was extracted by up to 300 ml of a solvent consisting of ether containing 3 per cent. v/v of nitric acid.   Reasonable quantities of uranium could be quantitatively extracted in 150 ml of this solvent.[3]   These were analysed by the double extraction technique with the results shown in Table IV.

TABLE IV

ANALYSIS OF SYNTHETIC MIXTURES CONTAINING URANYL AND THORIUM NITRATES

Sample	Uranium			Thorium		
	Present, g	Found, g	Difference, g	Present, g	Found, g	Difference, g
A	0·1613	0·1617	+0·0004	0·2824	0·2834	+0·0010
B	0·0865	0·0863	−0·0002	0·3764	0·3748	−0·0016

METHOD

SOLVENT PREPARATION AND RECOVERY—

The solvent for thorium nitrate extraction was prepared freshly by the slow addition of 12·5 ml of nitric acid, sp.gr. 1·42, to each 87·5 ml of peroxide-free ethyl ether.   The ether was prepared and recovered by the methods described in Part V of this series.[3]

PREPARATION OF THE CELLULOSE COLUMN—

The extraction tube and method of packing were the same as those described in Part V.[3] For a normal thorium extraction the column was packed in the solvent containing 12·5 per cent. v/v of nitric acid, but when a double extraction of both uranium and thorium was desired, the column was packed in ether containing 3 per cent. v/v of nitric acid.   The minimum length of column depended on the type of cellulose pulp used.   A column length of 5 cm was quite sufficient with pulp prepared from ashless tablets, although longer columns were used for most of the analyses quoted.   The controlling factor for the length of column was

found to lie in the retention of other metals rather than in the quantity of thorium to be extracted. The movement of yttrium nitrate was a useful guide to this hold-back, as it was found to be the most rapidly moving of the interfering metals usually associated with thorium in minerals; thus the movement of yttrium can be used to indicate the minimum length of column for any particular type of pulp.

PREPARATION AND TRANSFER OF SAMPLE—

As the original solution for extraction had to be phosphate-free, several methods of phosphate removal were investigated. The methods finally used were as follows—

(a) After solution of the sample, thorium, the rare earths, calcium, etc., were precipitated with oxalic acid, the precipitate treated with fuming nitric acid to destroy the oxalate radical and then dissolved in water. This procedure was particularly useful for low grade samples, where the oxalate precipitation also served as an enrichment stage.

(b) The monazite sand was treated by the method of Seelye and Rafter[4] with concentrated hydrofluoric acid and taken nearly to dryness on a steam-bath. Chemical decomposition of the sand took place, the thorium and rare-earth phosphates being converted to insoluble fluorides with the release of phosphoric acid. The physical appearance of the sand did not change as a result of this treatment, so that after addition of water the supernatant liquor was easily removed from the heavy sand particles by means of a polythene filter stick (see Fig. 2). Three treatments with water were sufficient to remove all traces of phosphate; the resulting product was then fused with potassium hydroxide and the melt leached with hot water. The residual hydroxides were filtered and dissolved in nitric acid.

Uranothorianites were usually soluble in hot nitric acid and did not contain phosphate; hence digestion of the sample with concentrated nitric acid was sufficient preliminary treatment.
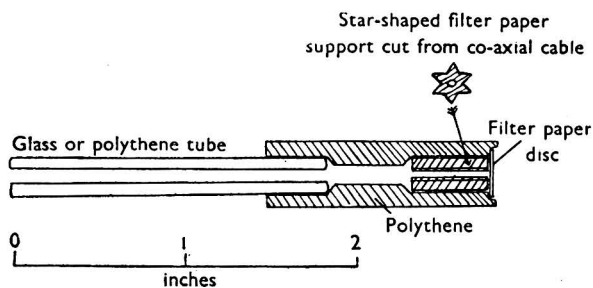
Fig. 2.   Polythene filter-stick

The strength of nitric acid in the original solution and its total volume were important factors in the efficiency of extraction. As observed in uranium extractions,[3] the movement of a number of impurities, particularly iron, was accelerated in higher acid concentrations. The volume of solution used had considerable effect on the volume of organic solvent needed.

For the transfer of the sample to the column the "wad" technique, as described in Part V,[3] was used for monazite sands. Uranothorianites gave a less viscous solution that could be poured directly on the top of the column.

THE EXTRACTION OF THORIUM—

The procedure for the extraction of thorium from monazites was the same as that already described for uranium in Part V,[3] except that the solvent used was ether containing 12·5 per cent. v/v of nitric acid. After the passage of 600 ml of solvent, ammonium hydroxide was added to the eluate to neutralise part of the acid, and the excess of solvent was distilled for recovery. Ammonium hydroxide was added to neutralise the remaining acid, and the solution was then re-acidified with hydrochloric acid. Oxalic acid was added to the boiling solution, the precipitated thorium oxalate filtered, ignited to ThO_2 and weighed.

For the analysis of uranothorianites, ether containing 3 per cent. v/v of nitric acid, sp.gr. 1·42, was first used until 150 ml of eluate had been collected; this extracted the uranyl nitrate. The receiving flask was changed, and 600 ml of the solvent of higher acidity was then passed through the column to extract the thorium nitrate. The uranium was estimated in the first fraction by ceric sulphate titration[5] after removal of the excess of solvent by distillation and conversion of the uranyl nitrate to sulphate by boiling with sulphuric acid in a Kjeldahl flask. The thorium in the second fraction was estimated by oxalic acid precipitation.

ANALYTICAL PROCEDURES

I. MONAZITE SANDS: FIRST PROCEDURE—

Weigh into a platinum dish sufficient sample to yield not more than 0·25 g of ThO_2, add 10 ml of hydrofluoric acid and evaporate nearly to dryness on a steam-bath. Add 20 ml of 5 per cent. hydrofluoric acid, warm, and remove the supernatant liquor with a polythene filter stick, Fig. 2, provided with a disc of Whatman No. 540 or 541 filter-paper. Repeat the complete hydrofluoric acid treatment twice, then wash the sample into a nickel crucible and remove the supernatant liquor as before. Add the paper disc from the filter-stick to the crucible and evaporate to dryness on a steam-bath. Add potassium hydroxide pellets corresponding to 5 times the weight of sample and remove excess of water from the alkali by placing the crucible under an infra-red lamp for 15 minutes; or, failing this, heat very gently over a low gas flame. Then fuse strongly for 45 minutes, although red heat is not necessary as the phosphate has been removed and the sand is less refractory than previously. Cool and transfer the crucible and lid to a 250-ml beaker and extract the hydroxides by boiling with 200 ml of water. Remove and wash the crucible and lid. Add a few grains of soluble starch to the suspension of hydroxides and boil. Cool and allow to stand for 5 minutes; the hydroxides should settle and leave a clear supernatant liquor. Remove the supernatant liquor to about 0·5 cm above the hydroxides with the aid of the polythene filter-stick and a disc of Whatman No. 541 paper. Add 200 ml of water, boil and allow to settle, removing the supernatant liquor as before. Should the filter-stick clog at any stage, replace the filter-paper disc and keep all discs used. Transfer all the discs to a 50-ml beaker, destroy the paper by digestion with 1 ml of fuming nitric acid and transfer to the main beaker. Add 20 ml of concentrated nitric acid to the main beaker and boil gently. The solution should clear; if not, add concentrated nitric acid until it does and then evaporate to dryness. Caution should be observed at this stage as occasionally a little zirconium phosphate settles out and causes bumping. Add 5 ml of water, 0·2 ml of concentrated nitric acid and 0·5 ml of 20-volume hydrogen peroxide. Warm on a steam-bath until all the red colour is discharged. Cool and add 2 ml of concentrated nitric acid.

Prepare a cellulose column 7·5 cm long, as previously described in Part V,[3] packing it in a solvent consisting of ethyl ether containing 12·5 per cent. v/v of nitric acid, sp.gr. 1·42. Add sufficient dry cellulose pulp to the sample solution, with stirring, to give a semi-dry mass; an addition of about 6 g is usually sufficient. Transfer this to the top of the column and beat up the "wad" so formed with a glass rod to form as continuous a part of the column as possible. Begin extraction with the solvent, transferring it at first via the sample beaker to wash it out. The column should never be allowed to run dry and the supernatant liquor should not exceed 10 ml. Collect the eluate in a 1-litre flask to a total of 600 ml. After the extraction, add slowly to the receiver 100 ml of water containing 30 ml of ammonium hydroxide, sp.gr. 0·880. Remove the excess of ether by distillation and transfer the acid solution to a 500-ml beaker and cool. Just neutralise with ammonium hydroxide, sp.gr. 0·880, add 25 ml of concentrated hydrochloric acid, make up the volume to about 400 ml with water and boil. Add 20 g of oxalic acid crystals slowly with stirring and allow to cool. Filter the precipitated thorium oxalate through a Whatman No. 42 filter-paper or Gooch crucible and wash the precipitate with 100 ml of a wash liquor consisting of 2 per cent. of oxalic acid in 0·1 N hydrochloric acid. Ignite the precipitate at 850° C and weigh as ThO_2.

II. MONAZITE SANDS: SECOND PROCEDURE—

Take a sample of the material containing not more than 0·25 g of ThO_2 into a sulphate or chloride solution. A pure monazite will dissolve readily after digestion in hot concentrated sulphuric acid; cruder samples containing highly refractory minerals will require fusion with potassium hydroxide as described in the first procedure, above. Adjust the acidity of the

solution to 0·5 N with hydrochloric or sulphuric acid, at the same time adjusting its volume to 200 ml, and then boil. Add 100 ml of boiling 25 per cent. oxalic acid solution with stirring. Allow to cool and filter through a Whatman No. 542 filter-paper, washing the precipitate with 2 per cent. of oxalic acid in 0·1 N hydrochloric acid. Wash the precipitate into a 100-ml beaker with water and evaporate to dryness. Add 20 ml of fuming nitric acid and evaporate to dryness; repeat the nitric acid treatment and evaporation. It is essential to destroy all traces of oxalate, as its presence in the column retards the extraction of thorium. Dissolve the dry nitrates in water, treat with hydrogen peroxide, add 2 ml of concentrated nitric acid and continue with the extraction and recovery as described in the first procedure.

III. URANOTHORIANITES—

Weigh 0·4 to 0·5 g of the finely ground sample into a 100-ml beaker, add 10 ml of concentrated nitric acid, cover with a watch glass, heat gently under reflux for 2 hours and then add 5 ml of water. This treatment usually gives a clear solution containing a little silica in suspension. If any heavy precipitate remains, remove it by filtration and fuse it with a few pellets of potassium hydroxide, extract the melt with hot water and transfer the hydroxides to the original solution. Evaporate the solution to dryness and dissolve the residue in 5 ml of water. Treat with hydrogen peroxide and add 2 ml of concentrated nitric acid as described above for monazite sands.

Prepare a cellulose column 15 cm long in ether containing 3 per cent. v/v of nitric acid, sp.gr. 1·42. Run out the solvent until there is no supernatant layer, then pour on the prepared nitrate solution and wash it into the column with more solvent from a wash bottle. Extract with 150 ml of the solvent, taking the same precautions as before, and collect the eluate in a 500-ml flask. Replace this receiver by a 1-litre flask and change the solvent to ether containing 12·5 per cent. v/v of nitric acid, sp.gr. 1·42, and extract with 600 ml.

To the first flask, which contains all the uranium and no thorium, add 100 ml of water and remove the ether by distillation. Determine the uranium by any suitable method, e.g., by ceric sulphate titration.[5] Determine the thorium in the second flask by oxalate precipitation as described in the first procedure, above.

RESULTS

Tables V and VI show a number of results by the methods described and by standard methods, viz., iodate - oxalate precipitation.

TABLE V

MONAZITE ANALYSES BY EXTRACTION COLUMN PROCESS

Sample and method	Sample weight, g	Weight of ThO_2 extracted, g	ThO_2 found, %		Results by standard methods, %
Procedure I—					
1	2·1241	0·2046	9·63	}	9·65
1	2·0387	0·1960	9·62		
2	2·5734	0·2398	9·32	⎫	
2	2·8578	0·2660	9·31	⎬	9·48
2	2·5499	0·2392	9·38	⎭	
2*	2·1247	0·1993	9·38		
3†	3·6834	0·2322	6·31	⎫	
3	3·5546	0·2215	6·23	⎬	6·0
3	3·0861	0·1956	6·34	⎭	
4	2·3061	0·1639	7·12		7·17
5	7·3105	0·0520	0·71		0·71
Procedure II—					
6	2·1225	0·2086	9·83		9·80
4	2·2677	0·1616	7·10	}	7·17
4	2·6095	0·1860	7·13		

* To this sample was added 0·1 g each of Y, Sc, Zr, Ti, Fe, Co, Ni, Cu, Pb and Sn before analysis. Tartaric acid, 3 g, was added to the original solution.

† The sample was of crude monazite that gave erratic results by the normal analytical procedure (*i.e.*, the iodate - oxalate method).

TABLE VI

ANALYSIS OF URANOTHORIANITE BY THE DOUBLE EXTRACTION PROCEDURE

		Uranium*			Thorium		
Sample	Weight of sample, g	Weight of U_3O_8 extracted, g	U_3O_8, %	U_3O_8 by standard methods, %	Weight of ThO_2 extracted, g	ThO_2, %	ThO_2 by standard methods, %
7	0·4589	0·1761	38·4	38·4	0·2491	54·3	53·7
7†	0·4711	0·1798	38·2	,,	0·2558	54·2	,,
8	0·4828	0·1703	35·3	38·5	0·2335	48·4	48·7
8	0·4938	0·1749	35·4	,,	0·2387	48·4	,,
9	0·4997	0·0682	13·7	13·3	0·3777	75·9	74·1
9	0·4676	0·0650	13·6	,,	0·3535	75·6	,,
10	0·4924	0·1301	26·4	26·4	0·2881	58·5	57·5

* Uranium was determined by titration with ceric sulphate in both the extraction and standard procedures.

† To this sample 0·1 g each of Fe, Mo, V, Ca, La, Nd, Sm, Ti, Zr, Ce, Co, Ni, Sn and Pb were added.

CONCLUSION

The work carried out, besides being the basis of a number of quantitative analytical techniques, has shown the possibilities of development on parallel lines of the extraction of a number of other metallic nitrates, such as scandium, zirconium and yttrium. Further, although previously limited to comparatively small quantities, indications are that the scale of the extractions can be increased, making the procedure useful for the preparation of extremely pure samples for research purposes.

This work has been carried out on behalf of the Ministry of Supply, and is published with the permission of the Ministry and the Director of the laboratory.

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NOTE—References 2 and 3 are to parts II and V of this series.

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The Determination of Copper in Steel by Internal Electrolysis

By D. L. CARPENTER and A. D. HOPKINS

Small amounts (10 to 25 mg) of copper as copper sulphate can be determined in presence of a great excess (5 g) of iron by the method of internal electrolysis. To determine copper in carbon steels, the sample is dissolved in a dilute sulphuric - hydrochloric acid mixture, absence of ferric iron being ensured by addition of hydrazine sulphate. Accurate results are obtained only if copper as copper sulphate is added to the solution before internal electrolysis. The method is as accurate as the routine iodometric method and takes less time to complete.

THE use of the method of internal electrolysis, *i.e.*, without the use of externally applied e.m.f., dates from the middle of the nineteenth century.[1,2,3] By this method it is possible to separate quantitatively small amounts of metals in presence of a preponderance of other metals. The apparatus is simple and robust and the method is often shorter than the more orthodox procedure and yet comparable in accuracy.

Sand[4] has given a description of the technique of internal electrolysis and quotes results obtained by various workers for the determination of silver in galena and pyrites, mercury in brass, bismuth and copper in lead, cadmium and nickel in zinc and small quantities of copper in the presence of large amounts of iron. Lurie and Ginsburg,[5,6] with an apparatus differing from Sand's in that no anode envelope was used, carried out a series of determinations of metals more noble than lead, *i.e.*, copper and bismuth in lead - zinc ores, and nickel, copper and cobalt in ores containing small amounts of these metals. The results were as accurate as those obtained by Sand.[4] Clarke, Wootten and Luke,[7] with an electrode system in which alundum shells were used instead of parchment paper as anode envelopes, determined bismuth and copper in lead alloys containing antimony and tin, and obtained accurate and consistent results.

The method of determination of copper in steel described by Fife and Torrance[8] appears to be accurate and less tedious than the routine iodine - thiosulphate method.[9] Using Sand's apparatus,[4] they found that, with sulphate solutions, 1 to 30 mg of copper could be determined in presence of 5 g of iron. In the presence of sulphuric acid, the iron was maintained in the ferrous state by the addition of hydrazine sulphate. The following method for copper in steel was given by these authors—

Dissolve 3 to 10 g of the steel sample in sulphuric acid, cool the solution, filter and neutralise with sodium hydroxide or ammonia. Add 3 ml of 96 per cent. sulphuric acid and an excess of hydrazine sulphate. The solution is then diluted and subjected to internal electrolysis. The authors state that the residue after filtration contains no copper.

In the following experiments confirmation of these results was sought. Sand's apparatus was used, first with a solution of copper and ferrous sulphates and then with copper-bearing steels of known analysis.

ANALYSIS OF SOLUTIONS OF IRON AND COPPER SALTS

APPARATUS—

The anode consisted of a thistle funnel, the stem of which was wound for a length of approximately 8 cm with 1-mm diameter iron wire. The anode was placed in a Whatman 16-mm by 100-mm diffusion cell, the top of which was bound tightly to the glass stem of the funnel. One end of the anode wire projected through the neck of the diffusion cell and was connected to the stationary cylindrical cathode of platinum gauze. The catholyte, contained in a 600-ml beaker, was stirred by a worm-ended glass rod driven by an electric motor, the glass rod passing axially through the cathode. The beaker was heated by a bunsen burner and the temperature of the liquid was measured by a mercury thermometer.

PROCEDURE—

The anolyte solution contained 5 g of iron as ferrous sulphate, 3 ml of 96 per cent. sulphuric acid and 0·2 g of hydrazine sulphate per 100 ml. The catholyte contained 5 g of iron as ferrous sulphate, 0·2 g of hydrazine sulphate and 3 ml of 96 per cent. sulphuric acid in a total volume of approximately 300 ml. Various quantities of copper were added to the catholyte in the form of a standard solution of copper sulphate. The absence of ferric ions was confirmed throughout the determination by testing the catholyte periodically with ammonium thiocyanate solution. The anolyte was poured through the thistle funnel into the diffusion cell and the anode assembly and platinum cathode were connected and fixed in position in the catholyte. The stirrer was switched on and the solution heated to 75° C. After 30 minutes, the beaker was lowered slowly while the cathode was washed with distilled water. The cathode was removed, washed with isopropyl alcohol and dried for 10 minutes in an air oven at 105° C. The weight of copper deposited and the colour and nature of the deposit were noted. Experiments to find the time needed for complete deposition of copper showed that the separation of copper was always complete after 30 minutes at 75° C.

RESULTS—

The results of the tests on solutions of copper and iron salts are shown in Table I. With

TABLE I

DEPOSITION OF COPPER FROM SOLUTIONS OF COPPER AND FERROUS SULPHATES

Expt.	Copper added, g	Copper found, g	Error, g	Error, per cent.
1	0·0250	0·0247	0·0003	1·2
2	0·0250	0·0246	0·0004	1·6
3	0·0200	0·0197	0·0003	1·5
4	0·0200	0·0194	0·0006	3·0
5	0·0150	0·0145	0·0004	2·7
6	0·0150	0·0145	0·0005	3·3
7	0·0100	0·0098	0·0002	2·0
8	0·0100	0·0097	0·0003	3·0

the exception of experiment 4, they show that the weight of copper deposited is within ±0·5 mg of the amount added and that the method is satisfactory for mixtures of salts.

DETERMINATION OF COPPER IN CARBON STEELS

ACID SOLVENT—

Fife and Torrance[8] state that the steel sample will dissolve in sulphuric acid. When this method of solution was attempted it was found (a) that solution in cold concentrated sulphuric acid, apart from an initial reaction lasting a few seconds, was extremely slow and (b) that sulphuric acid heated to fuming dissolved the sample slowly. A test in which 5 g of steel millings were treated with 50 ml of fuming sulphuric acid showed that, even after 2 hours' digestion, 59 per cent. of the sample remained unattacked. Unfortunately, this slow rate of solution is a serious limitation to the value of the method for routine analysis. Accordingly a solvent capable of more rapid solution of the steel was sought.

Fife,[10] in a recently published addendum to his original paper,[8] has stated that the sulphuric acid solvent consisted of the theoretical volume of 10 per cent. v/v sulphuric acid required to dissolve the steel plus 3 ml of 96 per cent. sulphuric acid in excess. However, in the present work, diluted sulphuric acid solutions ranging from 1 + 1 to 1 + 9 were found to be unsuitable. Although the reaction was fairly rapid, an insoluble residue remained and this contained an appreciable proportion (about three-quarters) of the total copper content of the sample. Nitric acid is unsuitable as a solvent; it will cause the formation of ferric ions. The following mixtures of hydrochloric and dilute sulphuric acids were found to dissolve steels completely in less than 45 minutes—

(a) 100 ml of diluted sulphuric acid (1 + 9) plus 10 ml of concentrated hydrochloric acid.

(b) 100 ml of diluted sulphuric acid (1 + 4) plus 10 ml of concentrated hydrochloric acid.

PROCEDURE—
Dissolve the steel millings in 100 ml of acid solvent.   Filter, neutralise with ammonium hydroxide and acidify with 3 ml of concentrated sulphuric acid.   Add an excess of hydrazine sulphate and dilute the solution to approximately 300 ml.   Then subject the solution to internal electrolysis for 30 minutes at 75° C in the same way as for the mixed salt solutions. Two steels of the following composition were used (the copper contents, determined by the iodine - thiosulphate method, were found to be 0·19 and 0·13 per cent. respectively)—

  0·19% *Copper steel*—C, 0·09%; Si, less than 0·01%; Mn, 1·05%; S, 0·248%; P, 0·035%; Ni, 0·084%.

  0·13% *Copper steel*—C, 0·09%; Si, less than 0·01%; Mn, 0·9%; S, 0·205%; P, 0·038%; Ni, 0·114%.

RESULTS—
The results obtained are shown in Table II; they show no uniformity.   High values are associated with a blackening of the copper deposit, subsequently proved to be due to the presence of iron.   The remaining results that are low indicate that deposition is incomplete, although the copper is not contaminated.   In all these experiments deposition did not begin immediately, an interval of approximately 10 minutes elapsing before copper appeared on

TABLE II

DETERMINATION OF COPPER IN STEEL

Acid solvent	Weight of sample, g	Copper in steel, %	Copper determined, %	Colour of deposit
(a)	5·0	0·19	0·13	Salmon-pink
(a)	5·0	0·19	0·13	Salmon-pink
(b)	5·0	0·19	0·22	Darkened
(b)	5·0	0·19	0·22	Darkened
(b)	5·0	0·19	0·19	Salmon-pink
(a)	5·0	0·13	0·15	Slightly darkened
(b)	3·0	0·13	0·13	Salmon-pink
(b)	3·0	0·13	0·18	Darkened

(a) 100 ml of diluted sulphuric acid (1 + 9) plus 10 ml of hydrochloric acid.
(b) 100 ml of diluted sulphuric acid (1 + 4) plus 10 ml of hydrochloric acid.

the cathode.   This induction period did not occur in the internal electrolysis of solutions of copper and iron salts.   Other experiments not recorded in Table II showed that increasing the time of deposition invariably resulted in blackening the deposit.   Possibly the presence of metals other than iron may be responsible for the variation in deposition of copper.

TABLE III

ANALYSIS OF STEEL SOLUTIONS CONTAINING ADDED AMOUNTS OF COPPER

Copper in steel		Copper added, g	Total copper found, g	Copper in steel, determined, per cent.
per cent.	g			
0·19	0·0095	0·0100	0·0195	0·19
0·19	0·0095	0·0100	0·0197	0·19
0·19	0·0095	0·0100	0·0199	0·20
0·13	0·0065	0·0100	0·0165	0·13
0·13	0·0065	0·0100	0·0166	0·13
0·13	0·0065	0·0100	0·0168	0·14

Accordingly, a solution of a steel sample was subjected to internal electrolysis in the normal way and gave a blackened copper deposit.   The contaminated copper was dissolved from the cathode and 0·0100 g of copper as copper sulphate solution was added to the catholyte. The catholyte was re-electrolysed for 30 minutes at 75° C, hydrazine sulphate being added as necessary.   A salmon-pink copper deposit weighing 0·0100 g was obtained.   Confirmation of this result was obtained by adding 0·0150 g of copper to a similar catholyte and getting a salmon-pink deposit weighing 0·0148 g.

Finally, known volumes of copper sulphate solution were added to the catholyte prepared from copper-bearing steels by dissolving 5 g of the steel in 100 ml of diluted sulphuric acid (1 + 4) and 10 ml of concentrated hydrochloric acid. The solution was filtered, neutralised with ammonia and 3 ml of concentrated sulphuric acid were added. An excess of hydrazine sulphate was added and the solution was diluted to 300 ml and subjected to internal electrolysis for 30 minutes at 75° C. The results are shown in Table III.

CONCLUSIONS.

In solutions containing only copper and iron sulphate from 10 to 25 mg of copper can be determined in presence of 5 g of iron by internal electrolysis with an error generally not exceeding $\pm0\cdot3$ mg.

Consistent results could not be obtained from solutions of copper-bearing steels when subjected to straight-forward internal electrolysis. However, by the addition of known amounts of copper sulphate solution to the catholyte before internal electrolysis, a satisfactory method has been developed for the determination of up to 0·2 per cent. of copper in 5-g samples. It is probable that the method can be used for determining larger quantities of copper.

The effect of the added copper sulphate solution in promoting the complete separation of the copper in steel is probably related to the concentration of free copper ions in the solution. The copper of the steel dissolves in hydrochloric-sulphuric acid mixtures as chlorocuprous acid, $H_2(Cu_2Cl_4)$, in which the copper exists mainly as complex anions, $(Cu_2Cl_4)''$ and $(CuCl_2)'$, the concentration of free cuprous ions being very low.[11]

In the absence of added copper sulphate, the current flowing will depend on the free cuprous ion concentration and the e.m.f. set up. The cell e.m.f. under these conditions will be equal to the anode potential, as the cathode potential will be nearly zero while the concentration of free copper ions is very small. The rate of neutralisation of copper ions, i.e., the cell current, will be very low, which results in a very slow rate of dissociation of the complex anions and an increased possibility of loss of copper owing to migration of anions. Addition of copper sulphate to the steel solution catholyte before internal electrolysis furnishes a relatively large concentration of free cupric ions. The copper begins to plate as soon as anode and cathode are connected and the positive $Cu - Cu''$ electrode potential is established, which leads to an increase in the cell e.m.f. and the current passing. The rate of removal of cuprous ions, and therefore the rate of breakdown of the complex anion, is then greater. Deposition of copper is complete and rapid, so that contamination by iron is avoided.

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The Photometric Determination of Aluminium in Magnesium Alloys by means of Solochrome Cyanine-RS

By A. BACON

Several German workers have described the use of Eriochrome Cyanine-R for the photometric determination of aluminium. This reagent was not available through the normal British supplies and Solochrome Cyanine-RS was suggested as the British equivalent. The paper describes the application of this reagent to the determination of aluminium in magnesium alloys containing alloying additions of aluminium in the ranges 0 to 0·35 per cent. of aluminium and up to 14 per cent. of aluminium, and also to the detection of trace amounts of aluminium up to 0·02 per cent.

Interference by zinc, nickel, manganese and cadmium is negligible; copper and iron interference is discussed in detail. The determination of aluminium in the presence of phosphate is also described. For alloying additions in the ranges stated, the method has an accuracy of ±1 per cent. of the maximum of the aluminium range covered. With metal containing less than 0·025 per cent. of aluminium the results are reproducible to ±0·0005 per cent. of aluminium.

MANY authors have described the use of Eriochrome Cyanine-R for the determination of aluminium. Snell and Snell[1] claim that 4 hours at room temperature or 1 hour at boiling temperature is required to attain a constant depth of colour at a pH of 3·8, although at higher pH (5·4 to 6·0) several days are required. This seems to be taken from a paper by Richter,[2] who also states that various preparations of Eriochrome Cyanine-R exhibit different reactions, which are expressed either in the character of the calibration graph or in different values for the lake. Two years earlier Rauch[3] had applied the same reagent to the determination of aluminium in magnesium alloys and had described sources of error experienced both in the photo-electric measurement and in developing the colour. Much of the work described in this paper was carried out in 1944, at which time Eriochrome Cyanine-R was not available from the usual sources of supply in England, but Solochrome Cyanine-RS was stated to be similar in properties. As early tests showed that the dye changed from red to yellow over the pH range of 3·0 to 8·0 and that aluminium salts reacted to form a purple lake, it was decided to investigate the reaction in detail and compare the results with the earlier reports on the Eriochrome Cyanine-R reagents.

Choice of filters—To select the most suitable colour filters, a solution containing 0·05 g of Solochrome Cyanine-RS per litre and an excess of an aluminium salt was buffered at pH 5·8 by means of sodium acetate and acetic acid, and the absorption measured on a Spekker absorptiometer at different wavelengths with Ilford colour filters and a tungsten filament lamp. The drum readings were plotted against the wavelength of maximum transmission of the colour filters. From Fig. 1 it can be seen that maximum sensitivity occurs with green filters. In the same figure is included an absorption curve of a solution containing only the reagent, and it is apparent that the dye alone absorbs strongly in the green waveband. At first it might be thought that by using yellow filters the blanks could be minimised, but in order to obtain a similar sensitivity in the yellow waveband, the amount of dye added would have to be increased approximately fourfold, resulting in a blank almost identical to that obtained with 0·05 g of dye per litre and green filters.

THE INFLUENCE OF pH ON COLOUR DEVELOPMENT—

In order to study the effect of pH on colour development and the stability of the solutions, a series of synthetic standards was prepared from pure magnesium sulphate and aluminium. Aliquots containing 0·5 mg of magnesium and various amounts of aluminium to represent a range of alloys of 0 to 20 per cent. of aluminium were transferred to 100-ml graduated flasks, and 10 ml of a 0·05 per cent. solution of Solochrome Cyanine-RS were added. The pH of the solutions was adjusted by adding 5 ml of 20 per cent. sodium acetate solution and appropriate amounts of N sulphuric acid. The solutions were finally diluted to 100 ml.

The absorption was determined on the Spekker absorptiometer with Ilford No. 604 green filters, tungsten lamp and 1-cm cells.   The pH of the solutions was measured with respect to a glass electrode.   The absorptiometer readings obtained after a 10-minute standing period were plotted against pH values and are shown in Fig. 2.   The colour formation occurs rapidly over the pH range 5·0 to 6·2; this is distinctly different from the slow reaction recorded by previous workers using Eriochrome Cyanine-R.   In order to determine whether the solutions were stable, readings were made on the absorptiometer after allowing the solutions to stand for a further hour, and the change in reading is shown in Fig. 3.   This curve shows that at pH 5·0 the solutions are unstable, and it is clear that the higher pH of 6·0 must be used if the solutions are to be sufficiently stable to permit a reasonable margin in timing.
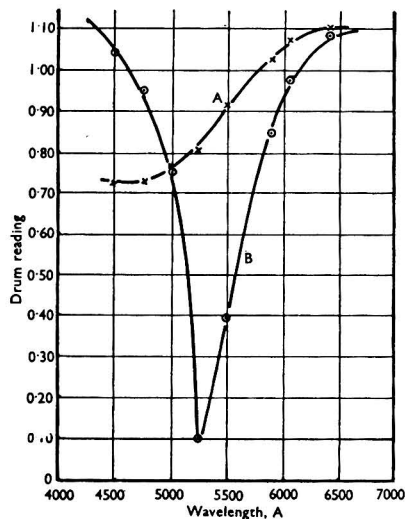
Fig. 1. Absorption by the dye and by the aluminium compound.   Ten-minute readings in 1-cm cells at pH 5·8 for (curve A) the dye at a concentration of 0·05 g per litre and (curve B) aluminium in excess.   Absorptiometer at water - water setting of 1·10

Numerous experiments were conducted at pH 6·1, but the results were persistently erratic.   At pH 5·8, however, excellent reproduction was obtained and all subsequent experiments were therefore conducted at this pH value.

Efficiency of the dye—The sensitivity of various preparations of the dye was compared by constructing a series of calibration graphs over the range 0 to 1 p.p.m. of aluminium with a constant concentration of 0·05 g of dye per litre.   These showed that the position of the calibration graph varied with the age of the dye preparation.   In aqueous solution, once the dye preparation has aged for 1 hour, no further movement of the straight portion of the calibration graph occurs for at least 15 days.   A similar effect occurs when the dye is prepared in dilute acetic acid.   When an attempt was made to simplify the procedure by dissolving the dye in a 20 per cent. solution of sodium acetate containing a little acetic acid (so that dye and buffer could be added in one operation), deterioration occurred so rapidly that the preparation became useless after a few hours.   The initial ageing of the dye was completely eliminated and its sensitivity increased by dissolving it in 0·001 N sodium hydroxide, but tests made after allowing the solution to stand showed that greater stability is obtained with an aqueous solution of the dye that has been allowed to age overnight.

The effect of temperature—The rate of fading was found to increase with increasing temperature.   For the greatest accuracy, therefore, the temperature of the reference solution and the sample solution after the final dilution to 100 ml should be identical and should not differ widely from that at which the calibration curve was obtained.

Reagent concentration for the range 0 to 0·8 p.p.m. of aluminium—The rate of fading of aluminium-free solutions increases with increasing dye concentration.   Introduction of

aluminium salts reduces the quantity of "free" reagent and, as the aluminium complex is perfectly stable, the solutions become more stable with increasing aluminium content.

This indicates that in order to reduce fading to a minimum, the quantity of dye used should not greatly exceed that necessary to cover the maximum concentration of the calibration range. To cover up to 0·8 p.p.m. of aluminium, a 1-cm cell in conjunction with a dye concentration of 0·10 g per litre is satisfactory. When 2-cm and 4-cm cells are used, which approximately reduce the maximum aluminium concentration to one half and one quarter, the concentration of dye is proportionately decreased.
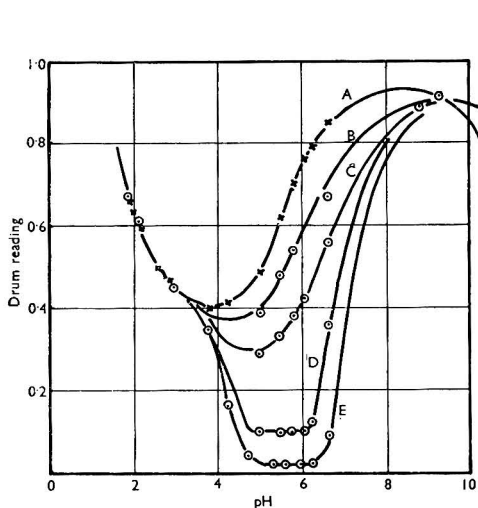
Fig. 2. The effect of pH on the absorption by the dye and aluminium compound. Curve A, no aluminium; curve B, 2·5 per cent. of aluminium; curve C, 5·0 per cent. of aluminium; curve D, 10·0 per cent. of aluminium; curve E, 20·0 per cent. of aluminium (i.e., 1 p.p.m.). Absorptiometer at water - water setting of 1·0
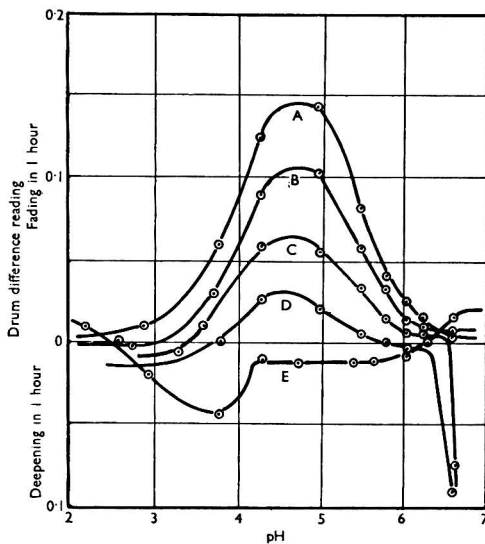
Fig. 3. Stability tests on synthetic standards. Curve A, no aluminium; curve B, 2·5 per cent. of aluminium; curve C, 5·0 per cent. of aluminium; curve D, 10·0 per cent. of aluminium; curve E, 20·0 per cent. of aluminium

Batch analysis—It is necessary to allow the solutions to stand for several minutes to permit the aluminium complex to form. As fading of the excess of dye occurs during this period, the same interval of time should elapse between colouring and reading each solution. This is conveniently achieved by introducing the dye, buffer and final water addition to each solution before proceeding to the next; by this means eight samples can be included in each batch, readings being started 10 minutes after colouring the first solution. For larger batches it is necessary to increase the time of standing and to calibrate accordingly.

Method of deriving differences—The influence of temperature and the age of the dye preclude the use of direct readings, and a difference method must be used. It was found that closer reproduction was obtained by deriving the differences during calibration to the 10, 5 and 2·5 per cent. of aluminium points and to derive the differences for the samples being analysed with respect to similar synthetic solutions.

The high absorption by solutions not containing aluminium necessitates a water to water setting of 1·50. We have found it more satisfactory to replace the right-hand water cell by a Wratten No. 74 green filter and set water to filter at 0·15.

METHOD FOR ALLOYS CONTAINING UP TO 14 PER CENT. OF ALUMINIUM

REAGENTS—

Sulphuric acid—Add 250 ml of sulphuric acid, sp.gr. 1·84, cautiously to 700 ml of water. Cool and dilute to 1 litre. Standardise against sodium hydroxide to 9·5 N.

Nitric acid, sp.gr. 1·2—Add 400 ml of nitric acid, sp.gr. 1·42, to 600 ml of water.

Colour reagent—Make an 0·05 per cent. solution of Solochrome Cyanine-RS in water, store in a dark bottle and pre-age overnight before use.

Buffer solution (a)—Dissolve 20 g of sodium acetate trihydrate in water, add 6 ml of N acetic acid and dilute to 100 ml.

Mercuric chloride solution—A 1 per cent. w/v aqueous solution.

SYNTHETIC STANDARDS—

Prepare three standards with the quantities of aluminium, magnesium sulphate and sulphuric acid shown in Table I. Add a small amount of a mercuric chloride solution to assist solution of the aluminium, and continue as described under "Procedure" to the 500-ml dilution.

TABLE I

COMPOSITION OF SYNTHETIC STANDARDS

Cell size	Aluminium, %	Aluminium, g	$MgSO_4.7H_2O$, g	$9.5 N$ H_2SO_4, ml
1 cm	10	0·05	4·55	15·55
2 cm	5	0·025	4·80	15·5
4 cm	2·5	0·0125	4·925	15·45

PROCEDURE—

Dissolve 0·5 g of alloy in 20 ml of 9·5 N sulphuric acid and 50 ml of water. Oxidise with 1 ml of nitric acid, sp.gr. 1·2, boil, cool, transfer to a 200-ml graduated flask and dilute to the mark. Transfer 10 ml to a 500-ml graduated flask and dilute to the mark.

Transfer 10 ml into a 100-ml graduated flask, dilute to about 60 ml with water and, according to the aluminium content, add (for 0 to 14 per cent.) 20 ml of colour reagent, (for 0 to 7 per cent.) 10 ml of colour reagent or (for 0 to 3·5 per cent.) 5 ml of colour reagent. Add immediately 5 ml of the buffer solution (a). Dilute to 100 ml and allow to stand for 10 minutes. Colour a 10-ml aliquot from the appropriate standard at the same time as the sample and in an identical manner.

Read the absorption in 1, 2 or 4-cm cells with Ilford No. 604 green filters and a tungsten lamp, the Spekker absorptiometer being set water to Wratten No. 74 green filter at 0·15, or alternatively set water to water at 1·50. Derive the difference in absorption between the sample and the appropriate synthetic standard and convert to percentage of aluminium by means of a calibration graph constructed in a similar manner.

CALIBRATION GRAPH—

Solution A: magnesium - aluminium solution—Dissolve 0·10 g of pure aluminium and 4 g of AnalaR magnesium sulphate, $MgSO_4.7H_2O$, in 15·7 ml of 9·5 N sulphuric acid and add 5 drops of mercuric chloride solution to assist solution of the aluminium. Add 1 ml of nitric acid, sp.gr. 1·2, and boil. Cool, transfer to a 1000-ml graduated flask and dilute to the mark. Transfer 25 ml to a 1000-ml graduated flask and dilute to the mark. One millilitre of this solution contains 0·0025 mg of aluminium, which is equivalent to 0·5 per cent. of aluminium on a 0·5-mg sample weight.

Solution B: magnesium solution—Dissolve 5·05 g of AnalaR magnesium sulphate, $MgSO_4.7H_2O$, in 15·4 ml of 9·5 N sulphuric acid. Add 1 ml of nitric acid, sp.gr. 1·2, and boil. Cool, transfer to a 200-ml graduated flask and dilute to the mark. Transfer 10 ml to a 500-ml graduated flask and dilute to the mark.

TABLE II

VOLUMES OF CALIBRATION SOLUTIONS

For 1-cm cell, take	Solution A ..	32	28	24	20	16	12	8	4	0	ml
	Solution B ..	2	3	4	5	6	7	8	9	10	ml
	Aluminium ..	16	14	12	10	8	6	4	2	0	per cent.
For 2-cm cell, take	Solution A ..	16	14	12	10	8	6	4	2	0	ml
	Solution B ..	6	6·5	7·0	7·5	8·0	8·5	9·0	9·5	10·0	ml
	Aluminium ..	8	7	6	5	4	3	2	1	0	per cent.
For 4-cm cell, take	Solution A ..	8	7	6	5	4	3	2	1	0	ml
	Solution B ..	8·0	8·25	8·5	8·75	9·0	9·25	9·5	9·75	10·0	ml
	Aluminium ..	4	3·5	3·0	2·5	2·0	1·5	1·0	0·5	0	per cent.

Preparation of calibration graphs—Transfer volumes of calibration solution according to Table II to 100-ml graduated flasks, and continue as in the Procedure. Derive differences with respect to the 10, 5 and 2·5 per cent. of aluminium solutions and construct calibration graphs. Typical calibration graphs are shown in Fig. 4. The readings obtained with the 10, 5 and 2·5 per cent. of aluminium calibration solutions should be identical with those of the corresponding synthetic standards.

SOURCES OF ERROR—

As small variations in the pH of the solution affect the intensity of the colours, the 20 ml of acid used to dissolve the sample must be controlled to within ±1 ml and should, therefore, be measured with a pipette or burette. Further, where synthetic solutions are used as reference standards, it is essential that the strength of the acid used in the analysis of alloys should be the same as that used to prepare the standards. The strengths of four
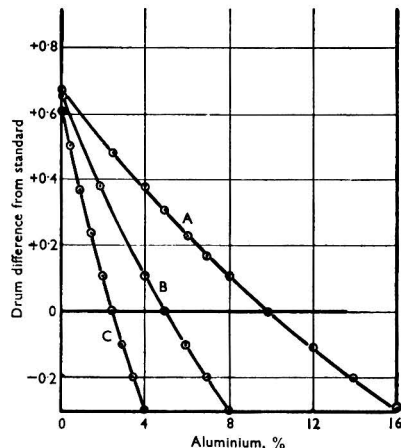
Fig. 4. Calibration graph for a temperature of 20° C at pH 5·8. Curve A, 1-cm cell, 20 ml of dye; curve B, 2-cm cell, 10 ml of dye; curve C, 4-cm cell, 5 ml of dye

samples of diluted sulphuric acid prepared by adding 1 volume of concentrated sulphuric acid, sp.gr. 1·84, to 3 volumes of water were found to vary between 9·5 N and 9·8 N; this 3 per cent. variation in normality introduces an error of about 0·05 per cent. of aluminium when 1-cm cells are used. When a fresh stock of acid is prepared it should, therefore, be titrated against standard alkali and its strength adjusted to coincide with that used to prepare the calibration graph and synthetic standards. If, however, an alloy is used as reference standard and the same acid is used for both sample and standard, the error introduced by such variation in normality is negligible, and titration of the acid against standard alkali is not essential.

The rate of fading of the blank with 20 ml of dye and 1-cm cells was found to be 0·10 drum divisions per hour, and the 10 per cent. of aluminium standard faded at the rate of 0·065 drum divisions per hour. If the solutions are allowed to stand for 5 minutes longer than they should during the initial standing period, errors in drum readings of approximately 0·009 and 0·005 will be introduced for the blank and 10 per cent. of aluminium, respectively, and this error in drum difference of about 0·004 is equivalent to about 0·08 per cent. of aluminium. Although such errors are undesirable, they are of less consequence than inaccurate timing of the individual samples, in which the error is not compensated by the same error in the standard. As the rate of fading decreases with increase of aluminium content, the closer the composition approaches to that of the standard the smaller will be the error introduced by inaccurate timing. It has been found that if the same supply of distilled water is used for the final dilution, the temperature variation over a batch of samples seldom exceeds ±0·5° C, and the error so introduced is negligible. In contrast, laboratory temperatures may vary considerably from day to day and the temperature of the water used for the final dilution should be adjusted to within ±5° C of the temperature at which the calibration curve was constructed.

The colour reproduction is also influenced by the accuracy of fractionation and it is desirable that, as far as possible, the same graduated glassware should be used for both the calibration and analytical procedure; this applies particularly to pipettes. As the dye will detect 1 part of aluminium in 100 million parts of solution, it is necessary to exercise great care to avoid contamination and, where aluminium alloys are analysed in the same laboratory, it is desirable to conduct the analysis of magnesium alloys in glassware specially reserved for the purpose. In order to avoid errors due to differences in absorption cells, the same cells should be used for calibration and analysis.

ACCURACY—

Over the range 5 to 14 per cent. of aluminium, when the above precautions were taken, differences were reproducible to ± 0.005 and usually to within ± 0.002. This corresponds to an accuracy of determination of ± 0.08 and ± 0.03 per cent. of aluminium. A proportionate accuracy was obtained for the ranges 2·5 to 7 per cent. and 1 to 3 per cent. of aluminium with the appropriate reference standards and absorption cells.

INTERFERENCES—

Under the conditions of analysis described, additions representing 10 per cent. of zinc, 20 per cent. of nickel, 50 per cent. of manganese or 50 per cent. of cadmium in the alloy did not give measurable absorptions.

Copper and ferric iron were found to produce colours with the dye that were similar to that produced by aluminium, but which exhibited maximum absorption at 5500 A and maximum colour formation at pH 7·0 and pH 4·0 respectively. At pH 5·8 the dye appeared to react more readily with aluminium than with copper or iron, as maximum interference by these metals was associated with minimum aluminium content, the greatest amount of dye then being available to form the copper and iron complexes. The error likely to occur from the concentrations of iron and copper normally experienced in magnesium alloys is negligible, and the calibration solutions need not contain iron and copper. Ferrous iron was found not to form a coloured compound with the dye.

Tartrates and citrates should be absent, as they inhibit the reaction with aluminium.

Phosphates interfere but, provided the concentration of P_2O_5 does not exceed 3 p.p.m., addition of phosphate to the calibration solutions is not essential. A calibration graph obtained with phosphate-free solutions has been successfully used to determine small amounts of aluminium remaining in the filtrate after separating the bulk of the aluminium as phosphate in acetic acid solution. For this purpose the filtrate was evaporated to a low bulk and the residual aluminium precipitated with ammonia. The precipitate was redissolved in hydrochloric acid, evaporated to fumes with sulphuric acid and, after adjusting the acidity, the aluminium was determined photometrically.

METHOD FOR ALLOYS CONTAINING UP TO 0·35 PER CENT. OF ALUMINIUM

In the range 0 to 14 per cent. of aluminium, the maximum concentration of aluminium that could be determined with 20 ml of colour reagent was 0·8 p.p.m. To adapt the procedure to the range 0 to 0·35 per cent. of aluminium entailed a change in the aliquot weight from 0·5 to 20 mg and also a reduction of the amount and strength of acid used to dissolve the sample to 5 ml of N sulphuric acid. This was insufficient for the purpose and recourse was made to a change in the buffer solution.

If the final aliquot is to be buffered at pH 5·8 by means of 5 ml of 20 per cent. sodium acetate solution, the maximum amount of N sulphuric acid that can be used to dissolve 0·5 g of alloy is 53 ml.

Since 50 ml can be simply and accurately measured with a pipette, this quantity was chosen, a small addition of acetic acid being made to the buffer to maintain the pH at 5·8.

REAGENTS—

Sulphuric acid—Add 27 ml of sulphuric acid, sp.gr. 1·84, cautiously to 900 ml of water. Cool and dilute to 1 litre. Standardise against sodium hydroxide and adjust to 1·0 N.

Nitric acid, 1·0 N—Dilute 62 ml of nitric acid, sp.gr. 1·42, to 1 litre.

Buffer solution (b)—Dissolve 20 g of sodium acetate trihydrate in water, add 1·65 ml of N acetic acid and dilute to 100 ml.

PROCEDURE—

Dissolve 0·5 g of alloy in 50 ml of N sulphuric acid.   Oxidise with 1 ml of N nitric acid, boil, cool and transfer to a 250-ml graduated flask.   Dilute to the mark.   Transfer a 10-ml aliquot to a 100-ml graduated flask and dilute to about 60 ml.   According to the aluminium content add amounts of colour reagent as follows—

> For 0 to 0·35 per cent. of aluminium, add 20 ml of colour reagent
> For 0 to 0·175 per cent. of aluminium, add 10 ml of colour reagent
> For 0 to 0·10 per cent. of aluminium, add 5 ml of colour reagent

Add immediately 5 ml of the buffer solution (b), dilute to 100 ml and set aside for 10 minutes.

Read the absorption in 1, 2 or 4-cm cells with Ilford No. 604 green filters, the Spekker absorptiometer being set water to Wratten No. 74 green filter at 0·15.   Take readings in the same way for the appropriate standard for the cell size used as given in the high-range method, using buffer solution (a).   Derive differences with respect to the appropriate standard and convert to percentage of aluminium from the high-range graph.   The figure so obtained should be divided by 40.

CALIBRATION GRAPH—

Aluminium - magnesium and magnesium solutions were prepared in the same way as for the high-range calibration, but with the ratio of aluminium to magnesium and the acid content recalculated to coincide with the low-range method.   Calibration graphs prepared with buffer solution (b) were found to be identical with those obtained for the high range. Similarly three synthetic standards containing 0·25, 0·125 and 0·0625 per cent. of aluminium gave readings identical with those of the high-range standards when the appropriate buffer solution was used.   It is unnecessary, therefore, to recalibrate for the low range of aluminium contents or to maintain an additional range of standards.

METHOD FOR SMALL AMOUNTS OF ALUMINIUM IN MAGNESIUM (LESS THAN 0·02 PER CENT.)

REAGENTS—

Reference solution—Dissolve 10 g of magnesium sulphate, $MgSO_4.7H_2O$, in water, add 16·6 ml of N sulphuric acid and 2 ml of N nitric acid and dilute to 500 ml.

PROCEDURE—

The procedure is the same as that described for alloys containing up to 0·35 per cent. of aluminium.   As the rate of fading increases with decrease of aluminium content, it is more satisfactory to derive differences to a solution not containing aluminium than to the reference standard containing the lowest aluminium content.

A 10-ml aliquot from the reference solution is used, therefore, to obtain differences for the extremely low aluminium contents, and the Spekker absorptiometer is set at a water to water setting of 1·0.

CALIBRATION GRAPH—

Calibration is made with the high-range calibration solutions (and the appropriate buffer solution), allowance being made for the factor of 40 relating to the aluminium content and differences being derived with respect to the zero calibration solution.   A setting of water to water of 1·0 is used.

INTERFERENCES—

Iron and copper also form coloured compounds with the dye at pH 5·8 and the influence of these elements on the aluminium determination was studied.   The interference by iron or copper increases as aluminium concentration decreases and is most serious, therefore, in the low aluminium range.   Since pH 5·8 is not the optimum for the formation of either the iron or copper complexes, the values obtained are erratic, the largest variation occurring in the iron values.   The interference when iron and copper are both present does not coincide with the sum of their individual absorptions, but depends upon the ratio of iron to copper. It is therefore impossible to correct accurately for the interference caused by iron and copper, but where the interference is relatively small in comparison with the aluminium absorption, an approximate correction is adequate.   The utility of such a correction will depend upon

the accuracy required, and in view of a possible error of 50 per cent. in the correction value, the percentage of aluminium to be deducted should not exceed twice the value corresponding to the permissible error. Hence, if it is required to analyse an alloy containing 0·01 per cent. of aluminium with an accuracy of ±5 per cent., the correction to be applied should not exceed 0·001 per cent. of aluminium, *i.e.*, 10 per cent. of the aluminium content. A correction graph for iron plus copper, when present in approximately equal amounts, is shown in Fig. 5. As an illustration of the use of the correction graph, suppose that an alloy
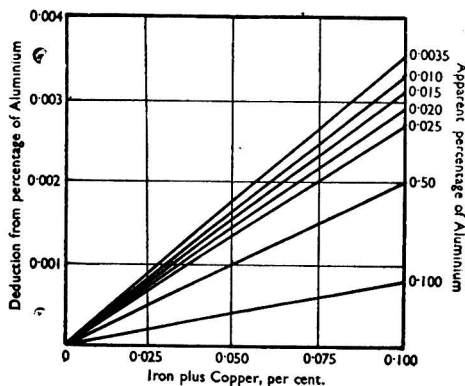
Fig. 5. Correction graph

containing 0·05 per cent. of copper and 0·05 per cent. of iron gave a drum difference of 0·155, which corresponded to an apparent aluminium content of 0·015 per cent. From the correction graph, the correction to be applied for 0·10 per cent. of iron plus copper at 0·015 per cent. of aluminium is 0·003 per cent. of aluminium, which gives a net value of 0·012 per cent. of aluminium. Since there is a possibility of a ±50 per cent. error in the correction, the value for the aluminium content may be in error by ±12·5 per cent. If the alloy contained 0·01 per cent. of iron and 0·01 per cent. of copper, the correction to be applied would be 0·0006 per cent. of aluminium and the value for the aluminium content would be within ±2 per cent. of the true value.

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Notes

EFFECTS DUE TO RESIDUAL NITRITE IN THE CANNING OF MEAT

A SEARCH of available literature has shown no published work on the subject of residual nitrite in the canning of meat beyond a brief statement by Thompson[1] that "with cured-meat packs an additional cause of pressure is possible with an over-liberal addition of nitrite to the pickle. This decomposes during retorting with liberation of gaseous oxides of nitrogen, and subjects the cans to pressures additional to those normally present." Thompson does not cite any published work or give any experimental data.

In this laboratory an investigation was recently made of the formation of "swells" in a batch of tongues canned in agar gel. The "swells" were obvious on removal from the retort, and persisted in this condition at room temperatures for several days. On reverting to normal appearance these cans had vacua of approximately 4 lb, as compared with 8 to 10 lb for normal cans.

It was found that "swells" were associated with the presence of gaseous oxides of nitrogen in the can atmospheres and with a high total-nitrite figure for the can contents (40 to 50 parts of sodium nitrite per million), as compared with normal can contents (20 to 30 p.p.m.). From the data it appeared that approximately 20 p.p.m. of nitrite were required for complete fixation of the haemoglobin and that any nitrite in excess of this would be residual. The possibility that some residual nitrite may have reacted with amino-acids derived from meat protein with the formation of elemental nitrogen has not been overlooked. The agar gel in the "swells" invariably contained nitrite (5 p.p.m. or more), while gel from normal cans contained no nitrite or less than 5 p.p.m.

In the pickling of the tongues, although an initial concentration of 0·06 per cent. of nitrite was aimed at, it is known that for the unsatisfactory batch this figure was exceeded, as the *used* pickle contained 0·08 per cent. of sodium nitrite and had a dirty brown - green colour. After discovery of the cause of the "swell" trouble, the amount of nitrite added to pickling solutions used for subsequent batches was reduced, and careful control of the amount was instituted. This resulted in satisfactory canned products. The used pickling solutions contained from 0·004 to 0·02 per cent. of sodium nitrite, and were of a clear red colour.

There is no doubt that the use of excessive quantities of nitrite in pickling was responsible for the "swells." The effect of this excess of nitrite on the colour of the pickling solution appears to confirm the observation of Callow[2] that, in the tank-curing of bacon with saltpetre, through the over-production of nitrite in the pickle by micro-organisms, the colour of the pickle may change from a clear red to a dirty brown or yellow, leading in extreme cases to discoloration of the bacon.

"Swells" that had reverted to normal appearance readily re-assumed a swollen condition on warming to about 50° C, and this fact, combined with the slow reverse action on cooling (already mentioned), indicated that the decomposition mechanism of nitrite to give "swells" was reversible in some way and possibly related to gelling and melting of the agar.

It was noticed during the study that nitrite in the agar gel of canned products, to the extent of some few parts per million, appeared to have a marked effect on the characteristics of agar gel. Gels containing no nitrite were firm and translucent, melting between 95° and 100° C, while gels containing nitrite were soft and transparent and melted in the region of 60° C.

Hydrolysis of the agar because of the acidity of gaseous oxides of nitrogen is unlikely to cause these effects, as gels with and without nitrite present had pH values of 5·9 to 6·1. Nitrite present in these gels did not appear to be present in a labile form, such as dissolved oxides of nitrogen, and it seems possible that the nitrite was combined in the form of a loose complex with the agar.

It is hoped to make a more detailed study of many interesting points raised by this preliminary investigation. The significant conclusion reached at this stage, however, is that residual nitrite present in canned meat to the extent of only some 20 parts per million as $NaNO_2$ may cause "swells" during processing.

This note is published by permission of the Government Analyst, Dunedin, and the Director of the Dominion Laboratory.

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THE PREPARATION OF STANDARD SOLUTIONS OF ALUMINIUM AND ZINC, AND OF CERTAIN OTHER METALS

THE dissolution of aluminium and zinc of high purity in diluted hydrochloric or sulphuric acid is a slow and tedious procedure, especially when the metal is in a compact form. The method has the further disadvantage that loss by spraying must be eliminated when the concentration of the standard solution prepared in this way is to be based upon the weight of the pure metal taken and, for solutions of aluminium and zinc, metal of high purity is probably the best reference substance that can be taken.

Dissolution in alkali, although less tedious, requires the same precaution to be taken and has the disadvantages of possible contamination of the solution from the vessel in which dissolution is effected and the introduction of alkali salts, whose presence in a solution may not always be desirable. Further, there is the unknown factor of aluminium as a probable impurity in the alkali hydroxide used.

In order to overcome these difficulties and to lessen the time required for preparing a solution, the following procedure was worked out first for aluminium and then for zinc. It is based on attack of the metal by liquid bromine.

Procedure for preparing a standard solution of aluminium—Heat a lump of "super-purity" aluminium of approximately the desired weight, 0·5 to 0·6 g is usually a suitable amount, in a small beaker with diluted hydrochloric acid (1 + 2) for several minutes to remove from the surface any adventitious iron that may have contaminated the metal during machining of the lump. Rinse the metal several times with distilled water, and dry it between pieces of filter-paper. Wrap the piece in aluminium foil and hammer it on a hardened-steel plate until it is flattened into a disc to give a larger surface of metal to be attacked. Remove the foil and place the piece of metal on the balance pan and weigh it accurately. If the purpose for which the aluminium is to be used justifies the refinement, correct this weight to "*in vacuo*." For 1 g of aluminium weighed in air with brass weights, this correction amounts to 0·00030 g.

Place the weighed piece of metal in a 100-ml Kjeldahl digestion flask and cover it with about 50 ml of distilled water. Insert a funnel in the mouth of the flask and, by means of a glass dropper, add 3 or 4 drops of freshly distilled liquid bromine to the flask. Shake and manipulate the flask so that the bromine comes into contact with the metal. Shake gently until all the liquid bromine disappears either by reaction with the metal or by dissolution in the water. Add 3 or 4 more drops of liquid bromine, shake, and allow time for reaction with the metal to take place. Proceed in this way until all the metal has dissolved.

Next, add about 1 ml of pure concentrated hydrochloric acid to the solution and warm to obtain a clear solution and to expel most of the excess of bromine. Remove and rinse the funnel and transfer the solution quantitatively to a 600-ml beaker.

Dilute to about 300 ml with distilled water, cover the beaker with a clock-glass, and boil the solution gently until the yellow colour of bromine disappears, and then boil for 10 or 15 minutes more. Removal of bromine can be accelerated and "bumping" can be avoided by first placing in the solution a piece of glass tubing longer than the diagonal of the beaker and containing a seal of solid glass at about 1 cm from the end that rests on the bottom of the beaker.[1] At the boiling-point of the solution a steady stream of bubbles rises from the bottom of the tubing and helps to remove bromine vapour and prevents "bumping." This device has been in general use in this laboratory for many years and can be strongly recommended.

Check for complete expulsion of free bromine by adding to the solution 1 drop of methyl orange indicator solution, which will no longer be decolorised when all free bromine has been expelled from the solution.

Cool the solution to room temperature, transfer it quantitatively to a 1-litre flask of accurately known content and dilute, with mixing, to the mark. Take the temperature of the well-mixed solution and correct the volume to the standard temperature of 20° C.

The bromine required for this method must be re-distilled in an all-glass apparatus to free it from traces of iron and from a white, insoluble deposit that remains in the distillation flask. As only 7 to 10 ml are required, this can be easily and quickly done.

The preparation of a standard solution of aluminium by this method can be completed in 4 or 5 hours, which is much quicker than dissolving a similar amount of super-purity aluminium in hot, diluted hydrochloric acid. There is no danger of loss by spraying and the manipulation demanded is easy and straightforward.

Zinc—The method for zinc is the same as for aluminium except that the metal need not be

flattened into the form of a disc.   Granulated zinc and zinc in pellet form dissolve quietly and smoothly when the bromine is added to them.   A pellet of forensic zinc, 1 g in weight, dissolved in 50 minutes.

BEHAVIOUR OF OTHER METALS WITH LIQUID BROMINE—

There is little doubt but that the method in its essential features can be applied to the preparation of standard solutions of some other metals, particularly of copper, antimony, bismuth, cadmium and tin, and it may be useful to record the behaviour of a few of them.

Antimony—Crystalline antimony in the form of rod dissolves readily and quietly when the bromine is added to the metal covered by diluted hydrochloric acid (1 + 1).   A 1-g piece of rod (ex-tartar emetic) covered by 25 ml of diluted hydrochloric acid (1 + 1) dissolved to give a clear solution in 15 minutes.   When no hydrochloric acid is present, reaction with the bromine is slow. A white incrustation, presumably of oxybromide, slows down the reaction.   When the metal is covered by concentrated hydrochloric acid, the reaction is too vigorous, being accompanied by occasional flashes of light.   The quieter reaction in the presence of the diluted acid is preferable. In the subsequent operations of transferring and diluting the solution (see procedure for aluminium) the ready hydrolysis of antimony halide solutions necessitates the use of diluted hydrochloric acid instead of water.

Bismuth—Dissolution with this metal is quiet, smooth and rapid, a bubble of gas rising occasionally to the surface of the covering layer of concentrated hydrochloric acid.   Two pieces of metal, etched first with concentrated hydrochloric acid and washed with 2 N hydrochloric acid and then water and dried, weighed 0·99 g and dissolved in 35 minutes.   As with antimony, the ready hydrolysis of bismuth halide solutions must be borne in mind in transferring and diluting the solution.

Cadmium—The granulated, acid-cleaned metal, weighing 0·97 g and covered by 30 ml of diluted hydrochloric acid (1 + 5), dissolved, without effervescence and with only an occasional bubble of gas being given off, in 35 minutes.   As with antimony and bismuth, this is a useful method of dissolution.

Copper—The metal as foil dissolves quickly and smoothly; 1 g of foil (B.D.H. Extra pure), folded into eight and covered by 25 ml of water, dissolved in 15 minutes.   In preparing a standard solution, the foil should first be etched and cleaned by treatment with nitric acid, washed with water and dried on filter-paper.

Gallium—Reaction between this metal and liquid bromine is too vigorous for the method described above to be used without danger of some loss of metal solution, and a variation in which gallium is exposed to moist bromine vapour has been worked out and will be described in a paper to be published on the determination of this metal.

Germanium—The method is not suitable for this metal, a white deposit, which does not dissolve readily, being formed even in the presence of diluted hydrochloric acid (1 + 1).

Magnesium—Magnesium wire covered by water reacts as soon as the bromine is added. There is some effervescence, but it is more controlled than that obtained with very dilute sulphuric acid; also, the chance of loss by the formation of a mist is less than with acid, and for these reasons this quieter reaction is preferred to dissolution in acid.   The wire, 0·1 g in weight, dissolved in 15 minutes.

Molybdenum—Reaction with molybdenum is slow; dissolution of 0·5 g of foil covered by 25 ml of diluted hydrochloric acid (1 + 1) was incomplete after 2 hours, but was complete after setting the system aside overnight.

Nickel—Attack by the bromine is slow, but not too slow to preclude the application of the method to preparing a standard solution; 0·5 g of metal was dissolved from a pellet of nickel, flattened into a disc by hammering between nickel foil, in 2½ hours.

Platinum—A piece of foil weighing 0·1580 g and covered by water lost less than 0·1 mg in weight after being in contact with liquid bromine in the cold for 2½ hours.   Even when covered with concentrated hydrochloric acid and liquid bromine and warmed, the loss in weight amounted to only 0·7 mg in 2 hours.

Rhenium—A few milligrams of the powdered metal dissolved quietly in a matter of minutes.

Rhodium—No action was apparent even on leaving the powdered metal in contact with the bromine for about 60 hours and the method is useless with this metal.

Tin—The vigour of the reaction varies markedly with the state of division of the metal. With powdered tin the bromine must be added carefully and in small amounts at a time if there is to be certainty of no loss occurring; 0·5 g of powdered metal (A.R.) covered by 30 ml of diluted

hydrochloric acid (1 + 5) dissolved in 15 minutes. With granulated tin, the reaction is quieter, but there is still need for caution in adding the bromine; 0·7 g of granulated metal covered by 30 ml of diluted hydrochloric acid (1 + 5) dissolved in 30 minutes. With "Spec-pure" metal, the reaction is quiet and smooth provided that the bromine is carefully added. A 1-g globule of this metal, covered by 30 ml of the diluted hydrochloric acid, dissolved in 45 minutes.

Tungsten—With 0·8 g of rod covered by water and in contact with liquid bromine for 4 days, there was no apparent action and the weight of the rod was unchanged.

Alloys—This method can also be used for dissolving certain alloys before analysis by well-known procedures. Four alloys of different type with approximate compositions ranging from copper 66 to 90, tin 1 to 4, lead 0·5 to 4 and zinc 1 to 30 per cent. dissolved quickly (0·5 g in 3 to 10 minutes according to the nature of the sample and its state of division) to give clear solutions in 30 ml of diluted hydrochloric acid (1 + 5) when bromine was added. If this is done carefully, the initial reaction, which may be vigorous, is easily controlled and there is no effervescence or mechanical loss; the lead and, of course, the tin remain in solution.

The times given above for the dissolution of the different metals, depending as they do on many factors, have no absolute significance. They do, however, give an indication of what can be expected of the method.

A feature of this method of attacking metals is the absence, except with magnesium, of effervescence and mist-formation, and special devices for obviating these sources of loss are no longer necessary.

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DETECTION OF BENZOIC ACID IN FOODS

AROMATIC polynitro compounds in acetone solution give colour reactions with alkali (Janovsky's reaction[1,2]). Benzoic acid on nitration responds to this test. In Mohler's test the *m*-dinitrobenzoic acid formed on nitration is reduced to *m*-diaminobenzoic acid, the ammonium salt of which has an intense reddish-brown colour in solution.

Benzoic acid is separated either by direct extraction or by steam distillation. It is finally obtained as the acid itself or the sodium or ammonium salt. The sodium and ammonium salts are usually obtained by shaking an ether solution of the acid with dilute sodium or ammonium hydroxide solution. The ammonium salt can also be obtained by the method described below; this method can also be used to purify crude benzoic acid residues.

A solution of the acid in 10 to 15 ml of ether is dried over anhydrous sodium sulphate and transferred to a dry test tube. A smaller test tube having a small opening on the side at about 2 cm from the bottom, containing a small amount of anhydrous sodium sulphate, 1 drop of strong ammonium hydroxide and a small plug of cotton wool, is fitted inside the larger tube (see Fig.). In a few minutes shining scales of ammonium benzoate separate out in the ether. This test is a modification of that first proposed by Leather.[3]

About 1 mg of the acid or the sodium or ammonium salt is nitrated by heating with 150 mg of potassium nitrate and 15 drops of sulphuric acid, sp.gr. 1·84, in a bath of boiling water for 20 minutes. The nitration is best carried out in a test tube. It is then diluted to about 30 ml and extracted once with 30 ml of ether. The ether layer is washed with two 10-ml portions of water and the ether removed by evaporation. The residue is dissolved in 2 ml of a mixture of 2 volumes of acetone and 1 volume of absolute alcohol, and 1 to 2 drops of
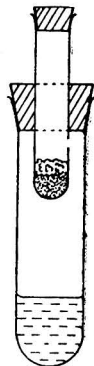
a 10 per cent. aqueous solution of sodium hydroxide are added.   On mixing gently a beautiful. purple colour develops and changes slowly to violet.

The colours obtained with p-hydroxybenzoic, p-chlorobenzoic, salicylic, cinnamic and phenyl- acetic acids and saccharin are as follows—

p-hydroxybenzoic acid	..	..	no colour
p-chlorobenzoic acid	..	..	reddish colour develops slowly
salicylic acid	..	..	no colour '
cinnamic acid	..	..	dirty violet changing to brown
phenylacetic acid ..	..	..	green
saccharin ..	..	..	no colour

Amounts of the order of 0·5 to 1 mg of benzoic acid give a strong reaction in the test.

The residue from the evaporation of the ether is not wholly soluble in the acetone - alcohol mixture; any insoluble matter is discarded.

To detect cinnamic acid in the presence of benzoic acid, the nitration is carried out as described, in a test tube, but 0·5 ml of nitric acid, sp.gr. 1·42, is used instead of the potassium nitrate - sulphuric acid mixture.   After heating for 20 minutes, the contents of the test tube are transferred to a small dish and evaporated to dryness on a water-bath.   The residue is dissolved in 2 ml of a mixture of acetone and alcohol, and 1 or 2 drops of sodium hydroxide solution are added.   Under these conditions only cinnamic acid gives a positive reaction (dirty violet colour changing to brown). No colour is obtained with benzoic acid.

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IMPROVEMENTS TO THE SILVER COBALTINITRITE METHOD FOR THE DETERMINATION OF POTASSIUM

IN the method of Klein and Jacobi,[1] flotation of the potassium silver cobaltinitrite precipitate with more than 200 μg of potassium leads to small errors that increase with the amount present. In spite of this, the method offers advantages over that of Ismael and Harwood[2] for tropical laboratories in that aqueous solutions are used at room temperature (25° to 30° C) instead of acetone and ether at 0° C.   It was found by the writer in Trinidad in 1945 that only one washing was necessary, and that if a 0·04 M solution of silver nitrate was used as wash liquid instead of water, the precipitate packed better and showed no tendency to slip, even in round-bottomed centrifuge tubes.   A further improvement was effected early this year when it was found that flotation, creep and sticking of the precipitate to the tube walls could be completely eliminated by including a detergent, such as "Teepol," in the silver nitrate reagent.   Combining the above with a modifica- tion of Mason's method[3] (flotation also occurs with Mason's precipitation technique) for developing a blue cobalt thiocyanate complex resulted in a rapid procedure that gave reproducible results in the hands of unqualified staff.

METHOD

REAGENTS—

Buffered silver nitrate solution—Mix 1100 ml of 0·2 N sodium acetate, 600 ml of 0·2 N acetic acid, 17 g of silver nitrate and 5 ml of Shell "Teepol," filter, and make up to 2000 ml.

Sodium cobaltinitrite solution—A 12·5 per cent. w/v aqueous solution, freshly made daily.

Ammonium thiocyanate solution—Dissolve 5 g of ammonium thiocyanate in 50 ml of water, filter, and make up to 100 ml with acetone.

Silver nitrate wash liquid, 0·04 M.

Sulphuric acid, 2 N.

PROCEDURE—

To an ammonia-free aqueous solution containing from 10 to 1000 μg of potassium in 2 ml, add 2 ml of buffered silver nitrate reagent.   Mix well by swirling and add 6 drops of 12·5 per cent.

w/v aqueous sodium cobaltinitrite, swirling after the first, second, fourth and sixth drops. Allow to stand at room temperature (15° to 30° C) for 15 minutes after adding the last drop. Centrifuge at 3000 r.p.m. and 17 cm radius for 3 minutes and then decant; allow the tube to drain for 2 minutes and wipe the inside rim with filter-paper. Pour in 2 ml of 0·04 M silver nitrate wash liquid, swirl, re-centrifuge and drain as before. Add 2 or 3 drops of 2 N sulphuric acid and heat in a bath of boiling water. If the precipitate does not dissolve in 5 minutes, heat directly in a small flame or on an open-wire hot-plate. When cool, add 5 ml of ammonium thiocyanate reagent for each 340 μg of potassium present. A stable blue colour appears at once and should be measured in a photo-electric absorptiometer within half an hour. If the tubes are corked immediately, the colours can be read at any time within at least 48 hours. No measurable blank is given by the reagents. Read the results from a calibration graph prepared in the usual way.

If the less volatile ethyl methyl ketone is available, it can replace acetone with advantage in the tropics—5 g of ammonium thiocyanate should then be dissolved in 60 ml of water, 40 ml of ketone added and the solution filtered.

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THE DETERMINATION OF THORIUM AND ITS SEPARATION FROM THE RARE EARTHS BY MEANS OF BENZOIC ACID

THE separation of thorium from the rare earths has received much attention and various reagents[1,2,3,4] have been recommended, all of which, with one or two exceptions,[5,6] require a double precipitation for the complete removal of rare earths present in significant quantities, as in monazite sand. In a search for a reagent that would effect a sharp separation from a large excess of the rare earths in a single operation we have re-investigated the conditions for precipitation by benzoic acid. This reagent for thorium was first used by Kolb and Ahrle,[7] but was later

TABLE I

EFFECT OF pH ON THE PRECIPITATION OF THORIUM WITH BENZOIC ACID
Weight of thoria taken = 0·0696 g

pH	Weight of thoria found, g	Error, mg
2·7	0·0696	——
2·4	0·0694	—0·2
2·2	0·0696	——
2·0	0·0694	—0·2
1·8	0·0692	—0·4
1·6	0·0687	—0·9

rejected by Neish,[8] who recommended *m*-nitrobenzoic acid. Neish's method was subsequently critically investigated and improved by Osborn.[9] The conditions for the determination of thorium and its separation from the rare earths of monazite by double precipitation with benzoic acid have recently been described by Venkataramaniah, Satyanarayanamurthy and Raghava Rao.[3] In this method a 1 per cent. solution of benzoic acid was used in a solution buffered with ammonium acetate to about pH 5·0. In a previous investigation of the precipitation of quadrivalent cerium in the presence of thorium and tervalent rare earths by potassium periodate[10] it was noticed that the relative concentrations of the hydrogen and the periodate ions played a definite role and that by increasing the periodate ion concentration, complete precipitation could be effected at higher hydrogen ion concentrations. Hence it appeared likely that by increasing the concentration of benzoic acid from 1 per cent. to 2 per cent., in a hot solution, a sharper separation of thorium from the rare earths might result, and this was substantiated by the following experiments.

EXPERIMENTAL

REAGENTS—

The ammonia used for neutralisation was re-distilled.
The benzoic acid and ammonium chloride conformed to recognised analytical standards.

PRECIPITATION OF THORIUM AND PROPERTIES OF THORIUM BENZOATE—

Precipitation of thorium under various conditions of acidity by a hot 2 per cent. solution of benzoic acid was first studied. The results are recorded in Table I. Below pH 1·8 the precipitation of thorium is incomplete.

Precipitated as described below, the thorium compound consists of coarse crystals that filter readily. Although the precipitate appears to be a definite compound, corresponding to the formula $(C_6H_5COO)_4Th$, direct weighing was not possible, for during the final washing with water, it had a tendency to hydrolyse, with formation of a basic compound.

ESTIMATION OF THORIUM AND SEPARATION FROM OTHER ELEMENTS

PROCEDURE—

To the thorium solution, or to the solution of thorium and other elements, containing not more than 0·1 g of ThO_2, add 10 g of ammonium chloride and dilute to 100 ml. Adjust the pH to between 2·2 and 2·6 by means of a pH meter, boil and add, with stirring, 100 ml of a 2 per cent. boiling solution of benzoic acid. The curdy precipitate that first forms becomes crystalline on boiling for 10 minutes and then settles rapidly. Set aside for 5 minutes, filter through a Whatman No. 41 filter-paper, wash with a hot 0·25 per cent. solution of the reagent and ignite the moist precipitate to ThO_2.

RESULTS—

Table II shows the results of applying this method to various quantities of thoria and Table III shows the separation of thoria from artificial mixtures with the rare earths.

TABLE II

ESTIMATION OF THORIUM BY BENZOIC ACID

Weight of thoria taken, g	Weight of thoria found, g	Error, mg
0·1044	0·1044	—
0·0457	0·0456	−0·1
0·0348	0·0350	+0·2
0·0069	0·0070	+0·1
0·0034*	0·0034	—
0·0017†	0·0017	—

* 50 ml of thorium solution plus 1 g of benzoic acid in 50 ml of boiling water.
† 25 ml of thorium solution plus 0·5 g of benzoic acid in 25 ml of boiling water.

TABLE III

SEPARATION OF THORIA FROM THE RARE EARTHS BY BENZOIC ACID

Weight of thoria taken, g	Weight of rare rare earths added, g	Weight of thoria found, g	Error, mg
(a) *Ceria earths*—			
0·1044	0·4470	0·1044	—
0·0696	0·8940	0·0695	−0·1
0·0696	1·3410	0·0698	+0·2
0·0348	2·2350	0·0348	—
0·0139	2·2350	0·0139	—
0·0069	1·3410	0·0070	+0·1
(b) *Yttria earths*—			
0·0696	0·1024	0·0696	—
0·0696	0·1536	0·0697	+0·1
0·0348	0·1024	0·0349	+0·1

Table IV shows the results obtained in the determination of thoria in the presence of various common elements. The impurities, which were added in the form of nitrates or chlorides, are calculated to the oxides.

TABLE IV

SEPARATION OF THORIA FROM COMMON ELEMENTS

Weight of thoria taken = 0·0696 g

Impurity	Amount, g	Weight of thoria recovered, g	Error, mg
BeO	0·2165	0·0696	—
MnO	0·1894	0·0697	+0·1
ZnO	0·2431	0·0694	−0·2
NiO	0·2055	0·0697	+0·1
CoO	0·1790	0·0694	−0·2
CuO	0·1860	0·0695	−0·1
CaO	0·2548	0·0696	—
SrO	0·1799	0·0696	—
BaO	0·2050	0·0695	−0·1
PbO	0·1860	0·0694	−0·2
CdO	0·2034	0·0697	+0·1
U_3O_8	0·1533	0·0696	—

APPLICATION TO THE DETERMINATION OF THORIA IN MONAZITE

Decompose a weighed sample with 70 per cent. perchloric acid, separate the resulting mixture of thoria and rare earths from phosphoric acid by double precipitation with methyl oxalate[4] and ignite the oxalate precipitate to oxide. Dissolve the mixed oxide precipitate in concentrated nitric acid with the addition of 1 to 2 ml of hydrogen peroxide to reduce cerium from the quadrivalent to the tervalent state and evaporate the solution almost to dryness on a water-bath. Take up the residue in water and determine the thoria by precipitation with a hot 2 per cent. solution of benzoic acid by the procedure described above.

The results of three analyses on a sample of monazite by this method were 8·25, 8·22 and 8·24 per cent.; Neish's *m*-nitrobenzoic acid method on the same sample gave 8·24 per cent. and the sodium naphthionate method gave 8·24 and 8·26 per cent.

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Ministry of Food

STATUTORY INSTRUMENTS*

1951—No. 2240.   The Food Standards (Edible Gelatine) (Commencement) Order, 1951.   Price 2d.

This Order, which came into force on December 23rd, 1951, appoints February 1st, 1952, as the date on which the standard for edible gelatine prescribed in the Food Standards (Edible Gelatine) Order, 1951 (S.I., 1951, No. 1196; Analyst, 1951, 76, 554) takes effect in respect of sales by retail.

——   No. 2241.   The Food Standards (Fish Paste) (Amendment) Order, 1951.   Price 2d.

This amending Order, which comes into force on March 7th, 1952, provides that the Food Standards (Fish Paste) Order, 1951 (S.I., 1951, No. 1456; Analyst, 1951, 76, 616) shall apply in relation to all sales instead of only in relation to sales by manufacturers and sales by wholesale.

——   No. 2242.   The Food Standards (Meat Paste) (Amendment) Order, 1951.   Price 2d.

This amending Order, which comes into force on March 7th, 1952, provides that the Food Standards (Meat Paste) Order, 1951 (S.I., 1951, No. 1457; Analyst, 1951, 76, 616) shall apply in relation to all sales instead of only in relation to sales by manufacturers and sales by wholesale.

British Standards Institution

NEW SPECIFICATIONS†

B.S. 1739:1951.   Filter Flasks.   Price 2s.
B.S. 1800:1951.   Methods for the Analysis of Raw Copper.   Price 5s.

DRAFT SPECIFICATIONS

A FEW copies of the following draft specifications, issued for comment only, are available to interested members of the Society, and may be obtained on application to the Secretary, Society of Public Analysts and Other Analytical Chemists, 7–8, Idol Lane, London, E.C.3.

Draft Specification prepared by Technical Committee OSC/7—Sampling Oils and Fats.
     CN(OSC) 6964—Draft B.S. for the Sampling of Fats and Fatty Oils (Revision of B.S. 627).

Draft Specification prepared by Sub-Committee DAC/3/1—Methods of Analysis of Milk.
     CN(DAC) 6961—Draft B.S. for Density Hydrometers for Use in Milk.

Draft Specification prepared by Sub-Committee DIC/–/3—Disinfectant Fluids.
     CN(DIC) 7302—Draft B.S. for Black and White Disinfectant Fluids.

Draft Specifications prepared by Technical Committee ISE/18—Sampling and Analysis of Iron and Steel.
     CN(ISE) 7329—Draft B.S. for the Determination of Molybdenum in Low Alloy Steels containing up to 0·5 per cent. Tungsten.
     CN(ISE) 7328—Draft B.S. for the Determination of Vanadium in Ferro-Vanadium.

Book Reviews

THE CHEMICAL ANALYSIS OF FOOD AND FOOD PRODUCTS.   By MORRIS B. JACOBS, Ph.D.   Second Edition.   Pp. xxiv + 902.   New York: D. Van Nostrand Company, Inc.   London: Macmillan & Co. Ltd.   1951.   Price $9·00; 67s. 6d.

The scope of this book has been enlarged compared with the first edition.   The second edition claims to include the application of analytical methods in the development and enforcement of standards of identity, purity or value, in problems of decomposition under storage conditions, in the improvement or control of the quality of natural and processed foods, in the determination of the nutritive value of foods for scientific, dietary or labelling purposes, in the technical control or supervision of raw materials and in problems of a toxicological or forensic nature.   These claims are to a great extent justified.

The material contained in the first edition has been largely retained, but much new matter has been added and some parts have evidently been rewritten.   Each chapter has been expanded and brought up to date; the latest references have been included.

* Obtainable from H.M. Stationery Office.   Italics indicate changed wording.
† Obtainable from the British Standards Institution, Sales Department, 24 Victoria Street, London, S.W.1.

There are twenty-one chapters; five new ones have been added and one has been omitted. Below are given the titles of the added chapters and a brief indication of their scope.

Chemical Food Poisoning—Acute and chronic poisoning and how it may be caused by poisonous vegetation, the use of insecticides, rodent poisons, etc., the solution of metals from utensils, contamination during manufacturing processes, and a section on detection and determination of poisons.

Vegetable Products—The examination and analysis of fresh, frozen and canned vegetables and nuts.

Flavour and Quality Measurement—In this chapter it is maintained that the acceptance of a food is closely related to the acceptance of its flavour; the factors contributing to preference for a given food are set out; a section is included on the measurement of flavour.

Filth and Decomposition in Foods—Contamination by insects, maggots, rodents, etc., and a section on the identification and determination of "filth."

Field Tests—Rough methods for use by inspectors to sort out suspicious samples.

A chapter on alcoholic beverages, which appeared in the first edition, has been omitted, and reference is made to a book that deals with this subject.

Like the first edition, the book is written with the American food legislation in view, but some reference is made to the food laws and the history of food legislation and adulteration in this country, *e.g.*, mention is made of the poisoning by arsenical beer that was widespread in and around Manchester in 1900.

In the review of the first edition, criticisms were made on some points. These criticisms have received attention and, in the main, do not apply to the present edition. The section on the freezing-point of milk, however, though it has been expanded a little, still does not receive the detailed treatment that its importance merits, while related subjects receive scant or no attention, *e.g.*, the vital subject of the standardisation of thermometers is discussed in a dozen lines and omitted altogether from the index.

The type is larger and more distinct than in the first edition, and the paper is good. The tests are set out better, an improvement that facilitates reference. Proof reading has been well done.

The first edition was considered by the reviewer to be a book that would be of great service in the analysis of foods. The changes and additions made in the second edition enhance its value in this respect.   J. R. STUBBS

THE PRACTICE AND SCIENCE OF BREADMAKING. By D. W. KENT-JONES, Ph.D., B.Sc., F.R.I.C.,
    and JOHN PRICE. Second Edition. Pp. x + 278. Liverpool: The Northern Publishing
    Co., Ltd. 1951. Price 25s.

The first edition of this work was published in 1934, and there can be no doubt that a new edition was called for. The book is written for the trade, not for the analyst or scientist; it does achieve its objective of explaining "a difficult problem simply" and of being "of assistance to those bakers and students who are really trying to take an intelligent interest in their important national task." Of what value is this book to the chemist? The following synopsis will show the scope, and it will be seen that chemists, who frequently have to investigate trade practice without having detailed knowledge of that trade, will find much in this book to give them the theory behind the general sound practice of the craftsman. A very short history of breadmaking is given, and then an explanation of what wheaten bread is; the authors next deal with the raw materials used in breadmaking, the important factors concerned in panary fermentation, special apparatus used for dough testing, the many and varied types of breadmaking processes, modern bakery machines and ovens, a brief review of bakehouse management and the laws and regulations dealing with bakery practice. From the practical man's point of view, one of the most valuable chapters deals with bread faults, particularly the summary tables of these facing page 126. Bakers and bakery students will find these tables of immense value for reference. Also from the practical man's viewpoint, valuable readily-available information will be found on recipes for bread, on different fermentation methods and on fermented confectionery.

The chemist outside the trade will find brief descriptions of the more popular machines now in use for testing doughs, mainly by rheological methods, and a chapter on the nutritive value of bread, written from a general stand-point and not from the narrowness of the brown *versus* white bread controversy. Finally, there is a chapter on analytical work, but this of a very elementary nature—properly so, because it is designed for the baker and not for the bakery chemist.

A number of criticisms of this work could be made by chemists—for example, there is no clear distinction made between adsorption and absorption; in the discussion of dough changes there is no mention of the real factors affecting the rheological properties, namely the stretching and relaxation of the dough piece; in making standard sodium carbonate solution there is no instruction to ignite, and there is the use of a factor of 1·021 for a standard solution. In the reviewer's opinion, however, such criticisms are not justified with a book of this type. The reader must read this purely from the stand-point of practice or refer to it for information on bakery procedure.

The book is well printed and typographical errors are few.   C. W. HERD

Publications Received

EXPERIMENTAL SPECTROSCOPY. By RALPH A. SAWYER, Ph.D., Sc.D. Second Edition. Pp. x + 358. London: Chapman & Hall Ltd. 1951. Price 30s.

THE DIAGNOSIS OF MINERAL DEFICIENCIES IN PLANTS BY VISUAL SYMPTOMS. By T. WALLACE, C.B.E., M.C., D.Sc., F.R.I.C. Second Edition. Pp. vii + 108 + 312 colour plates + Index. London: H.M. Stationery Office. 1951. Price 35s.

HORMONES: A SURVEY OF THEIR PROPERTIES AND USES. Pp. xii + 220. London: The Pharmaceutical Press. 1951. Price 35s.

ORGANIC SYNTHESES. Volume 31. Editor-in-Chief: R. S. SCHREIBER. Pp. vi + 122. New York: John Wiley & Sons Inc. London: Chapman & Hall Ltd. 1951. Price $2.75; 22s.

FURTHER LABORATORY AND WORKSHOP NOTES. Compiled and edited by RUTH LANG, Ph.D., A.Inst.P. Pp. xii + 290. London: Edward Arnold & Co. 1951. Price 28s.

STATISTICAL METHODS FOR CHEMISTS. By W. J. YOUDEN. Pp. x + 126. New York: John Wiley & Sons Inc. London: Chapman & Hall Ltd. 1951. Price $3.00; 24s.

INVESTIGATION OF THE USE OF CHEMICALS IN FOOD PRODUCTS. Union Calendar No. 1139. 81st Congress, 2nd Session Report No. 3254. Pp. 11. Washington: U.S. Government Printing Office. 1951.

CHEMICALS IN FOOD PRODUCTS. Hearings before the House of Representatives Select Committee to Investigate the Use of Chemicals in Food Products. Pp. v + 582. Washington: U.S. Government Printing Office. 1951.

THE C.I.E. INTERNATIONAL COLOUR SYSTEM EXPLAINED. By G. J. CHAMBERLIN. Pp. 34. Salisbury: The Tintometer Ltd. 1951. Price 5s.
    A simple explanation of the International System for the description of colour, written for the non-technical reader, and showing its value for colour specification in industry.

THE NATURE OF FOWL NEPHRITIS. By W. G. SPECTOR, M.A., M.B., B.Ch., M.R.C.P. Agricultural Research Council Report Series No. 11. Pp. iii + 16. London: H.M. Stationery Office. 1951. Price 3s. 6d.

TRACE ELEMENTS IN PLANT PHYSIOLOGY. Pp. xix + 144 + 10 plates. Waltham, Mass.: The Chronica Botanica Co. London: Wm. Dawson & Sons Ltd. 1950. Price $4.50; 36s.
    A symposium organised by the International Union of Biological Sciences at the Rothamsted Experimental Station with a Report of the Proceedings by T. Wallace, C.B.E., M.C., D.Sc., F.R.I.C., and a Foreword by J. M. Sirks. (Lotsya, Vol. 3—I.U.B.S. Colloquia, Series B, No. 1.)

ANALYSIS OF ELECTROPLATING AND RELATED SOLUTIONS. By K. E. LANGFORD. Pp. xi + 369. Electroplating and Metal Finishing, 83/85 Udney Park Road, Teddington, Middx., England. 1951. Price 52s.

A TEXTBOOK OF PRACTICAL ORGANIC CHEMISTRY, INCLUDING QUALITATIVE ORGANIC ANALYSIS. By A. I. VOGEL, D.Sc., D.I.C., F.R.I.C. Second Edition. Pp. xxiii + 1033. London: Longmans, Green & Co. 1951. Price 50s.

A TEXTBOOK OF QUANTITATIVE INORGANIC ANALYSIS, THEORY AND PRACTICE. By A. I. VOGEL, D.Sc., D.I.C., F.R.I.C. Second Edition. Pp. xxiii + 918. London: Longmans, Green & Co. 1951. Price 48s.

Notice to Authors

THE Society publishes papers concerned with all aspects of analytical chemistry, inorganic and organic, including chemical, physical, biological, bacteriological and micro-methods. Papers on these and allied subjects, by members of the Society or by non-members, may be submitted for publication; they may—

(1) record proposals for new methods and the·investigations on which the proposals are based;

(2) record the results of original investigations into known methods or improvements therein;

(3) record analytical results obtained by known methods where these results, by virtue of special circumstances, such as their range or the novelty of the materials examined, make a useful addition to analytical information;

(4) record the application of new apparatus and new devices in analytical technique and the interpretation of results.

(5) record minor investigations or kindred matter and descriptions of new apparatus and its applications, which may be accepted for publication under their respective section headings.

Communications—Papers and all communications relating thereto should be sent to the Editor of *The Analyst*, 7–8, Idol Lane, London, E.C.3.

Papers will normally be submitted to at least one referee, by whose advice the Publication Committee will be guided as to the acceptance or rejection of any communication.

Papers accepted by the Publication Committee must not be published elsewhere except by permission of the Committee.

Synopsis—All papers must be accompanied by a short synopsis of about 100 to 250 words indicating the scope and results of the investigation, and an appraisal of the accuracy of any new method proposed. Contributions intended for publication in the "Notes" or "Apparatus" sections do not require synopses.

Proofs—The address to which proofs are to be sent should accompany the paper. Proofs should be carefully checked and returned within 48 hours.

Reprints—Twenty-five reprints, or a maximum of fifty if there is more than one author, are supplied gratis. Additional reprints may be obtained at cost if ordered directly from the printers, W. Heffer & Sons Ltd., Hills Road, Cambridge, at the time of publication. Details are sent to authors with the proofs.

NOTES ON THE WRITING OF PAPERS FOR "THE ANALYST"

Manuscript—Papers and Notes should be typewritten with double spacing and on one side *only* on non-absorbent paper. Two copies should be sent to the Editor, and a further copy retained by the author. A duplicate sketch or tracing of all figures should be included for office use. Manuscripts should be in accordance with the style and usages shown in recent copies of *The Analyst*.

The title should be brief but descriptive.

Conciseness of expression should be aimed at; clarity is facilitated by the adoption of a logical order of presentation, with the insertion of suitable paragraph or sectional headings.

Descriptions of new methods should be supported by experimental data showing their precision and selectivity.

Generally, the best order of presentation is as indicated below—

(*a*) Synopsis.

(*b*) Statement of object of investigation and, if necessary, historical introduction.

(*c*) Preliminary experimental work.

(*d*) Description of method. Working details of proposed methods are most concisely and clearly given in the imperative mood, and should normally be given in this form. *e.g.*. "Dissolve 1 g of sample in 10 ml of water and add . . ." Well-known procedures must not be described in detail.

(*e*) Presentation of results.

(*f*) Scope and validity of results.

(*g*) Conclusions, and if required, a short summary of the principal results.

Tables, diagrams, etc.—The number of tables should be kept to a minimum. Column headings should be brief. Tables consisting of only two columns may often be arranged horizontally. No lines should be ruled in tables in the manuscript. Tables should be supplied with titles and be so set out as to be understandable without reference to the text.

Tables or graphs may be used, but not both for the same set of results, unless important additional information is given by so doing.

In general, graphs should have a reasonable number of co-ordinate lines, and not only the two main axes. Graphs consisting of straight lines passing through the origin, such as calibration curves, should not be submitted: instead, an equation should be given in the text. Graphs should be prepared in the same manner as other diagrams.

Diagrams and graphs should be drawn in Indian ink on Bristol board, stout paper or tracing cloth, not larger than foolscap size. The use of squared paper should be avoided if possible, as it often leads to poor reproduction. Red, orange or brown ruled paper must not be used; if it is necessary to use ruled paper, blue or green rulings may be used, as these colours do not reproduce in block-making. All lettering should be inserted lightly in black lead pencil at the appropriate place on the diagram, and will be replaced by type in block-making. All lines in Indian ink should be firmly drawn and sufficiently thick to stand reduction. If the artist is uncertain in his free-hand work on graphs, he should submit a careful pencil drawing that can be traced.

Drawings should be specially prepared for submission to *The Analyst*, as they cannot normally be returned, and may be modified or cut in the course of block-making.

Photographs—Photographs for reproduction on art paper should be submitted in the form of glossy prints made to give the maximum detail.

Abbreviations—Normality and molarity are generally expressed as decimal fractions (*e.g.*, $0.02\,N$, $0.375\,M$). Abbreviational full stops are omitted after the common contractions of metric units (*e.g.*, ml, g, μg, mm) and after ° C, ° F, μ, A and other units represented by symbols; litre and metre, when without prefixes, are printed in full.

Abbreviations of words other than recognised units should be avoided in the text; symbols and formulae are not used instead of the names of elements and compounds in the text, but may be used in addition to names where it is necessary to avoid ambiguity, *e.g.*, to specify crystalline composition, as in $CuSO_4.5H_2O$, to show structure, or in equations.

Percentage concentrations of solutions should be stated as "per cent. w/w" (alternatively "g per 100 g"), as "per cent. w/v" (alternatively "g per 100 ml"), or as per cent. v/v. Concentrations of solutions of the common acids, however, are often conveniently given as dilutions of the concentrated acids; they should then be given in the form "diluted hydrochloric acid $(1 + 4)$," which signifies 1 volume of the concentrated acid mixed with 4 volumes of water. This avoids the ambiguity of 1:4, which might be equivalent to *either* $1 + 4$ *or* $1 + 3$.

References—References should be numbered serially in the text by means of superscript figures, *e.g.*, Dunn and Bloxam[1] or Allen,[2] and collected in numerical order under "REFERENCES" at the end of the paper. They should be given, with the authors' initials, in the following form—

1. Dunn, J. T., and Bloxam, H. C. L., *J. Soc. Chem. Ind.*, 1933, **52**, 189T.

2. Allen, A. H., "Commercial Organic Analysis," Churchill, London, 1882, p. **123**.

For books, the publisher, and place and date of publication should be given, followed by volume or page number, or both if required.

Authors are recommended, in their own interests, to check their lists of references against the original papers; second-hand references are a frequent source of error.

———————

Neglect of any of the points mentioned above is likely to cause delay in publication.

Further useful advice to authors is contained in the Royal Society's publication entitled "General Notes on the Preparation of Scientific Papers," published for the Royal Society by the Cambridge University Press, price 2s. 6d.

CHEMIST with bacteriological experience required at Cambridge Factory or Bacteriologist prepared to work on Industrial Effluent disposal. Salary according to qualifications and experience. Write (quoting Ad. 574) stating age, experience and salary required to Personnel Manager, Pest Control Limited, Bourn, Cambridge.

A VACANCY exists for a male chemist for analysis of cast iron and related materials. Age preferably 20 to 27. Previous analytical experience of ferrous alloys an advantage. Salary £234–£475 per annum according to age, experience and qualifications. Applications should be sent to British Cast Iron Research Association, Bordesley Hall, Alvechurch, Birmingham.

THE GEIGY COMPANY LTD. requires an assistant Chemist, minimum age 24, who will be responsible to the Work's Analyst for the testing of a wide range of raw materials. The salary offered will depend on education, qualifications and experience, but will not be less than £400 per annum. Applications, giving full details, should be addressed to the Labour Officer, Tenax Road Works, Trafford Park, Manchester, 17.

CHEMIST (male or female) required for laboratory of large engineering works in West London area. The work involves analysis of ferrous and non-ferrous alloys and investigation of various problems in connection with metal finishing and corrosion. 5-day week; pension fund; good prospects for advancement. Write Box No. 3801, THE ANALYST, 47, Gresham Street, London, E.C.2.

IMPERIAL CHEMICAL INDUSTRIES LIMITED has a vacancy in one of its Divisional laboratories for a chemist to take charge of research on analytical methods. Applicants must possess an Honours Degree in Chemistry and have practical experience and a knowledge of modern analytical technique. Salary according to experience and qualifications. Applications should be made to the Recruitment Section, Central Staff Department, Imperial Chemical Industries Limited, Imperial Chemical House, Millbank, London, S.W.1.

ANALYST–CHEMIST required for the laboratory of a large light electrical engineering works in the West London area. Applicants should have had experience in metal finishing processes and general process control. Degree standard required. Write giving details of age, qualifications and experience to Box No. 3799, THE ANALYST, 47 Gresham Street, London, E.C.2.

LABORATORY ASSISTANT (Female), aged between 18 and 30 years, required for the laboratory of a large electrical engineering company in the West London area. Intermediate standard preferred and previous experience of routine chemical analysis essential. Write giving details of age, qualifications and experience to Box No. 3800, THE ANALYST, 47, Gresham Street, London, E.C.2.

QUALIFIED ANALYTICAL CHEMISTS required for Assay Laboratory of a Northern Rhodesian Copper Mine. Starting basic salary £55 per month plus fluctuating cost of living allowance now about £8 per month. Life Assurance and Contributory Pension Scheme. Cash Bonus Scheme which at present rate equal to 60% cf basic salary. Outward passage paid. Apply giving full details of age, qualifications and experience to Foster Turner & Everetts Ltd., Box No. 3030/1, 11, Old Jewry, London, E.C.2.

GLAXO LABORATORIES LTD. require in their Analytical Department at Greenford an Assistant preferably with experience in industry or in a public analyst's laboratory. Starting salary in the neighbourhood of £500 per annum according to experience and/or qualifications. Contributory pension fund and incentive bonus schemes. Applications in writing to Senior Personnel Officer, Glaxo Laboratories Ltd., Greenford, Middlesex

THE ROYAL BOROUGH OF KENSINGTON

APPOINTMENT OF PUBLIC ANALYST (PART-TIME)

THE Royal Borough of Kensington invite applications from suitably qualified persons for the appointment of Public Analyst (Part-time).

The person appointed will be paid in accordance with the fees fixed by the Joint Negotiating Committee for Public Analysts (Part-time).

Conditions of appointment may be obtained on written application to me.

Applications to be received within fourteen days of the publication of this advertisement.

J. WARING SAINSBURY,
Town Clerk.

TOWN HALL,
KENSINGTON, W.8.

ASSISTANT DEVELOPMENT CHEMIST (with or without experience) is required by Development Section of Pest Control Ltd., Cambridge. The work is concerned with the manufacture of synthetic organic chemicals, and involves Laboratory Research, Plant Investigations, starting up of new plants, and Pilot Plant work. The position offers experience and opportunities for energetic man interested in Chemical Manufacture. Candidates should have at least passed Higher Certificate or its equivalent, and salary will depend on age, qualifications, and experience ranging between £200 and £400 per annum. Write (quoting Ad. 582), stating age, qualifications, etc., to Personnel Manager, Pest Control Limited, Bourn, Cambridge.

UNIVERSITY OF BRISTOL. Applications are invited for the post of Micro-Analyst in the Department of Organic Chemistry. Some familiarity with organic microanalytical techniques is essential. One day each week may be devoted to the development of analytical methods. Salary according to age and experience. Applications, giving age, general qualifications and experience, should be sent to The Registrar, The University, Bristol, 8.

STAFFORDSHIRE COUNTY COUNCIL

COUNTY CHEMICAL LABORATORY, STAFFORD

APPOINTMENT OF ASSISTANT ANALYST

APPLICATIONS are invited for the above-mentioned appointment from candidates having a University Degree and/or the Associateship of the Royal Institute of Chemistry. The salary scale is £570 per annum, rising by annual increments of £15, £15, and £20, to a maximum of £620 per annum. Further particulars can be obtained from the County Medical Officer of Health, County Buildings, Stafford, and the last date for the receipt of applications will be *7th March*, 1952.

T. H. EVANS,
Clerk of the County Council.

COUNTY BUILDINGS,
STAFFORD.
19th January, 1952.

DEARNE VALLEY WATER BOARD

APPOINTMENT OF CHEMIST AND BACTERIOLOGIST

APPLICATIONS are invited for the above position in accordance with the Scheme of Conditions of the National Joint Council for Local Authorities' Administrative, Professional Technical and Clerical Services Grade V (a) (£600/£660 per annum).

The successful candidate will be required to have specialised knowledge and experience of the treatment of chemical and bacteriological examination and analysis of, public water supplies, and also to technically supervise a Lime/Soda Treatment Plant for 750,000 gallons per day.

The appointment will be subject to the Local Government Superannuation Act, 1937, and to the passing of a medical examination, and will be terminable by one month's notice on either side.

Applications, stating age, qualifications, experience, present and previous appointments, and endorsed "Chemist and Bacteriologist," are to be sent to the undersigned with copies of three recent testimonials by 9 a.m. on 25th February, 1952.

Candidates must disclose whether to their knowledge they are related to any member or senior officer of the Board and canvassing, either directly or indirectly, will disqualify.

W. R. HUDSON,
Clerk of the Board.
Waterworks Offices,
Wombwell, nr. Barnsley.
21st January, 1952.

ANALYTICAL CHEMISTS are invited by the Ministry of Supply to apply for a post in the grade of Principal Scientific Officer or Senior Scientific Officer at a Research Establishment in London to lead a team investigating new methods of analysis. Experience of such work is essential, and a bias towards organic analysis would be an asset. Candidates should have a 1st or 2nd Class Honours Degree, or equivalent qualification in Chemistry, with considerable research experience. Salary will be assessed according to age, qualifications and experience within the ranges: Principal Scientific Officer (minimum age 31), £1,000 to £1,375 p.a.; Senior Scientific Officer (minimum age 26), £750 to £950 p.a.; rates for women somewhat lower. The post is unestablished but carries benefits under F.S.S.U. Application forms obtainable from the Ministry of Labour and National Service, Technical and Scientific Register (K), Almack House, 26, King Street, London, S.W.1. Quoting F.40/52/A. Closing date 29th February, 1952.

FOR SALE: Hilger's Spekker Photoelectric Absorptiometer, Model H560, in good working condition. Box No. 3798, THE ANALYST, 47, Gresham Street, London, E.C.2.

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CONTENTS   *Page*